**Supporting Information for**

# A $10^6$-fold Enhancement in $N_2$-binding Affinity of an $Fe_2(\mu\text{-}H)_2$ Core upon Reduction to a Mixed-valence $Fe^{II}Fe^{I}$ State

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## NMR Spectra

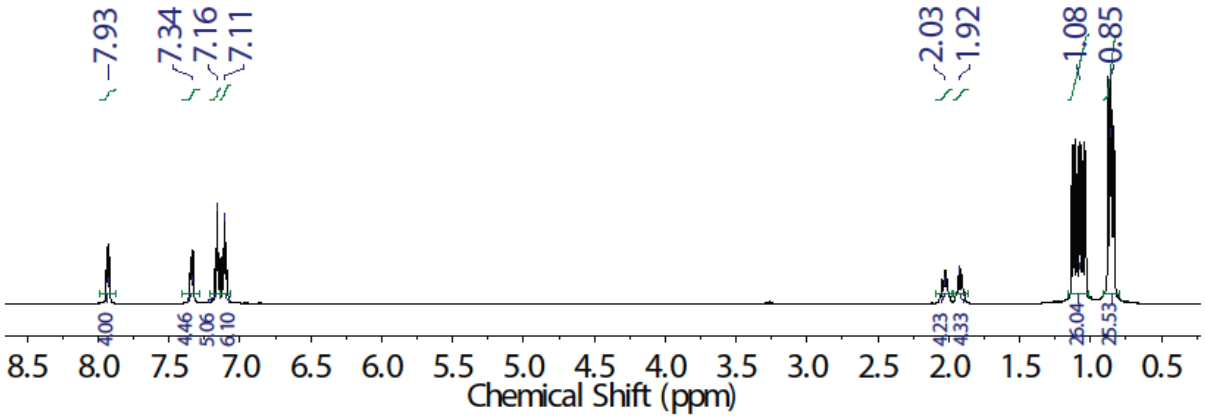


**Figure S1.** $^1$H NMR spectrum (500 MHz, 298 K) of **2** recorded in $C_6D_6$.

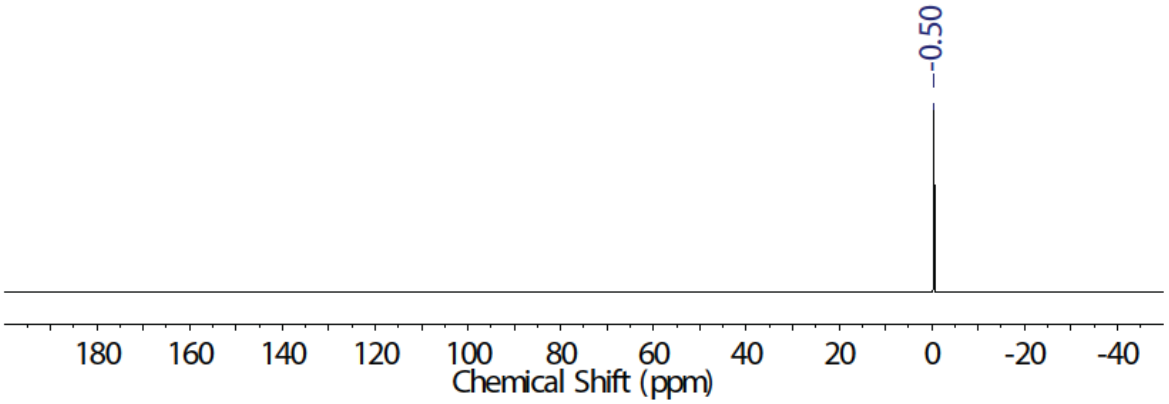


**Figure S2.** $^{31}$P NMR spectrum (202.4 MHz, 298 K) of **2** recorded in $C_6D_6$.

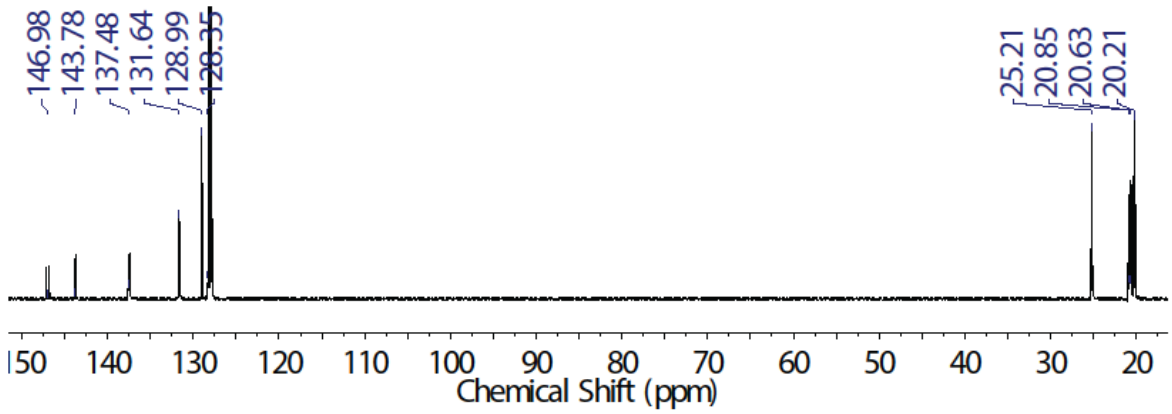


**Figure S3.** $^{13}$C NMR spectrum (125.7 MHz, 298 K) of **2** recorded in $C_6D_6$.

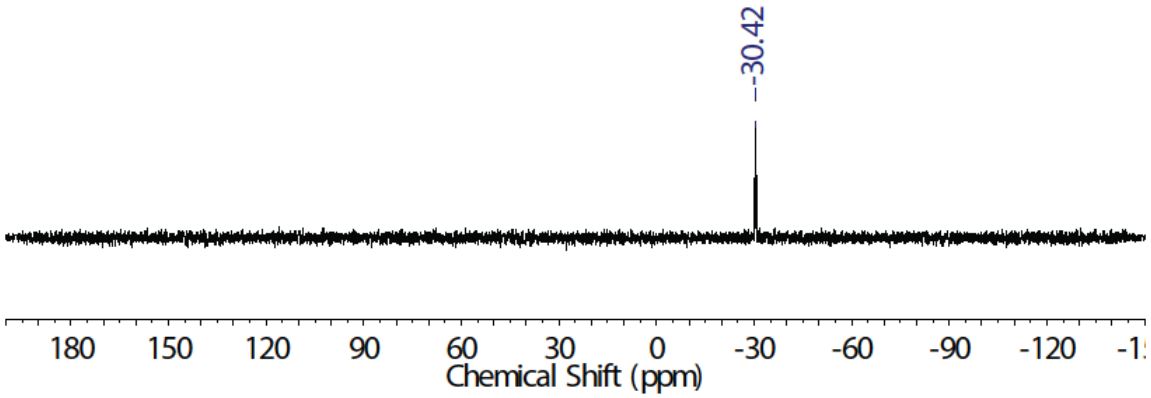


**Figure S4.** $^{29}$Si NMR spectrum (99.3 MHz, 298 K) of **2** in $C_6D_6$.

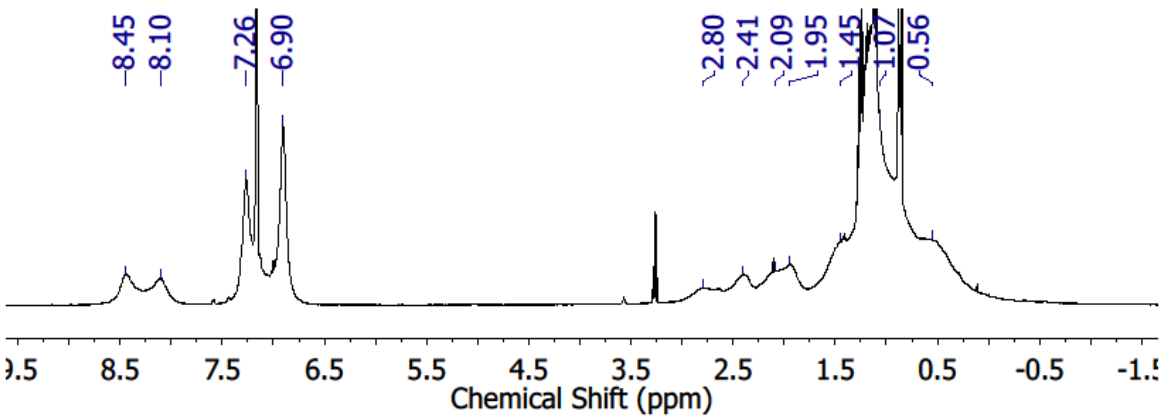


**Figure S5.** $^{1}$H NMR spectrum (500 MHz, 298 K) of **3-N$_2$** in $C_6D_6$ under 1 atm $N_2$.

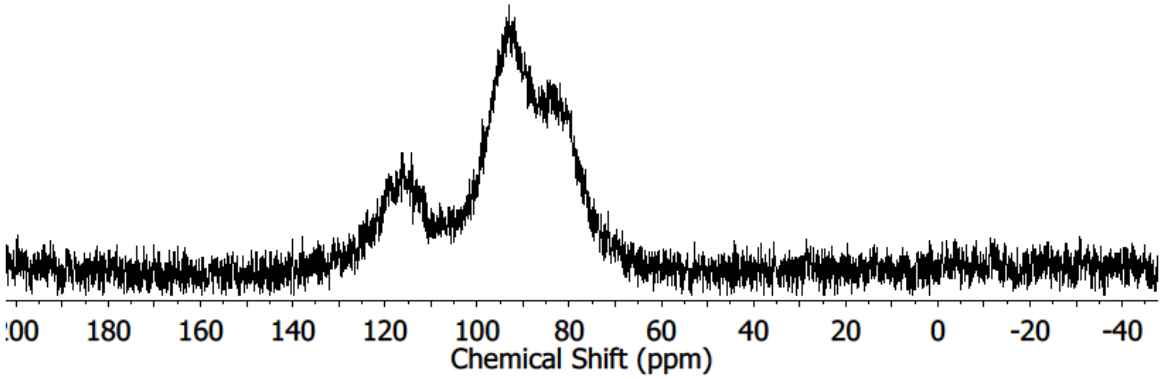


**Figure S6.** $^{31}$P NMR spectrum (202.4 MHz, 298 K) of **3-N$_2$** in $C_6D_6$ under 1 atm $N_2$.

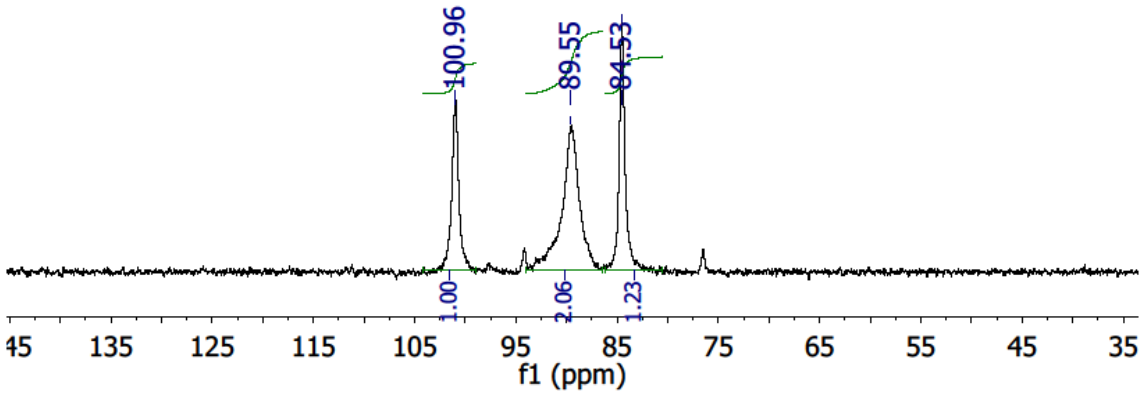


**Figure S7.** $^{31}$P NMR Spectra (202.4 MHz, 203 K) of **3-N$_2$** in toluene-$d_8$ under an argon atmosphere.

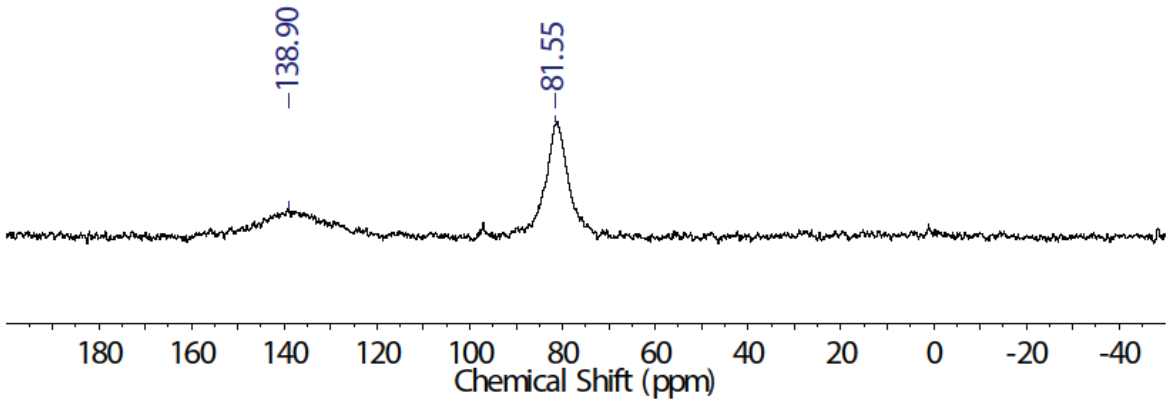


**Figure S8.** $^{31}$P NMR Spectra (202.4 MHz, 353 K) of **3-N$_2$** in toluene-$d_8$ under an argon atmosphere. While the $^1$H NMR spectrum collected at this temperature (see figure S13) is indicative of a symmetric molecule, the large chemical shift separation between the two $^{31}$P resonances suggests that the coalescence temperature for these nuclei is much higher. Effectively, the 'NMR timescale' for the $^{31}$P nuclei is much shorter than that of the $^1$H nucleus.[4]

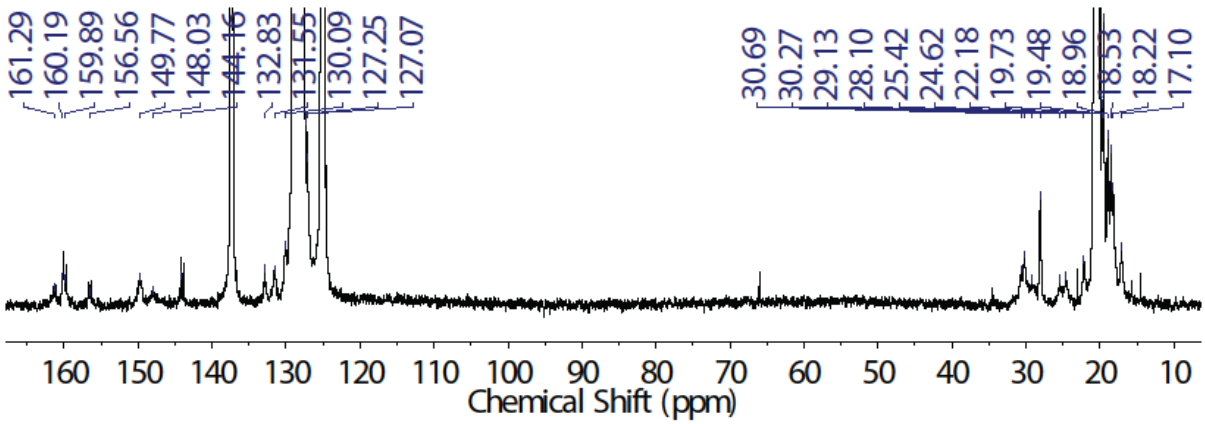


**Figure S9.** $^{13}$C NMR spectrum (125.7 MHz, 223 K) of **3-N$_2$** recorded in $C_7D_8$ under an argon atmosphere.

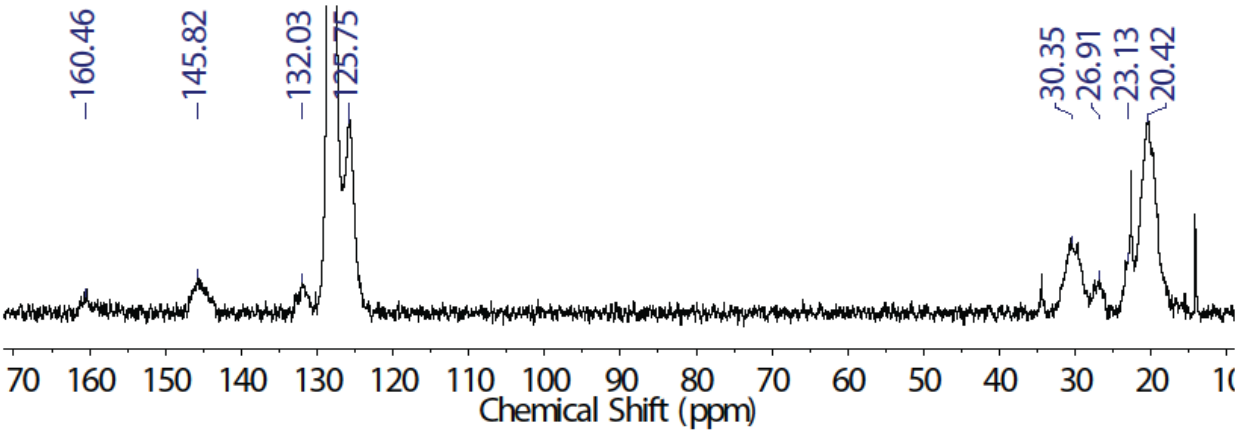


**Figure S10.** $^{13}$C NMR spectrum (125.7 MHz, 323 K) of **3-N$_2$** recorded in toluene-$d_8$ under an $N_2$ atmosphere.

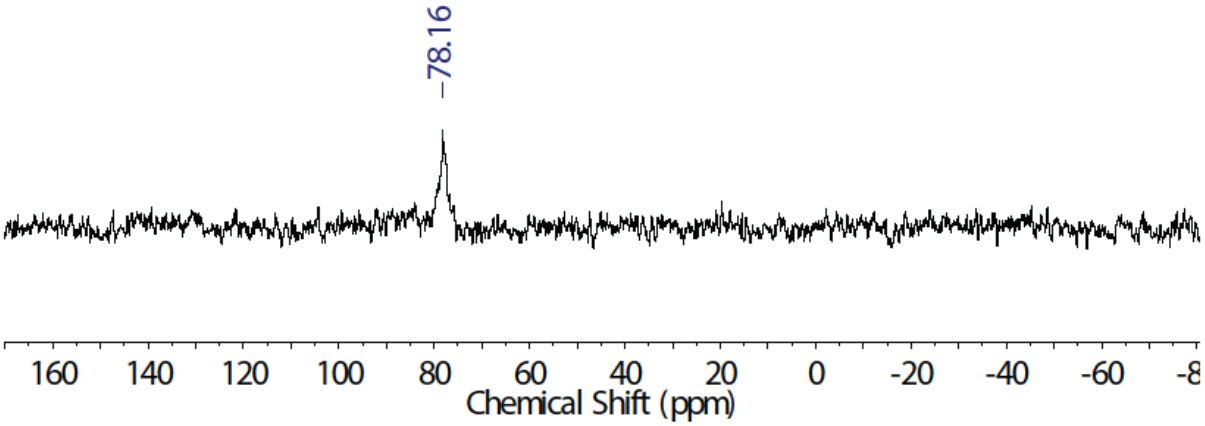


**Figure S11.** $^{29}$Si NMR spectrum (99.3 MHz, 223 K) of **3-N$_2$** in toluene-$d_8$ under an Ar atmosphere.

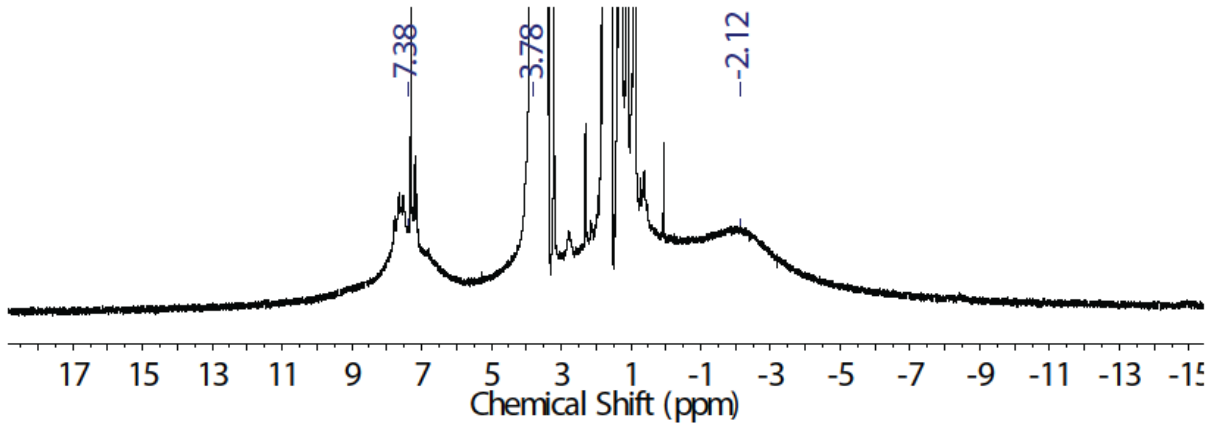


**Figure S12**. $^{1}$H NMR spectrum (300 MHz, 298 K) of **4-$(N_2)_2$** recorded in THF-$d_8$.

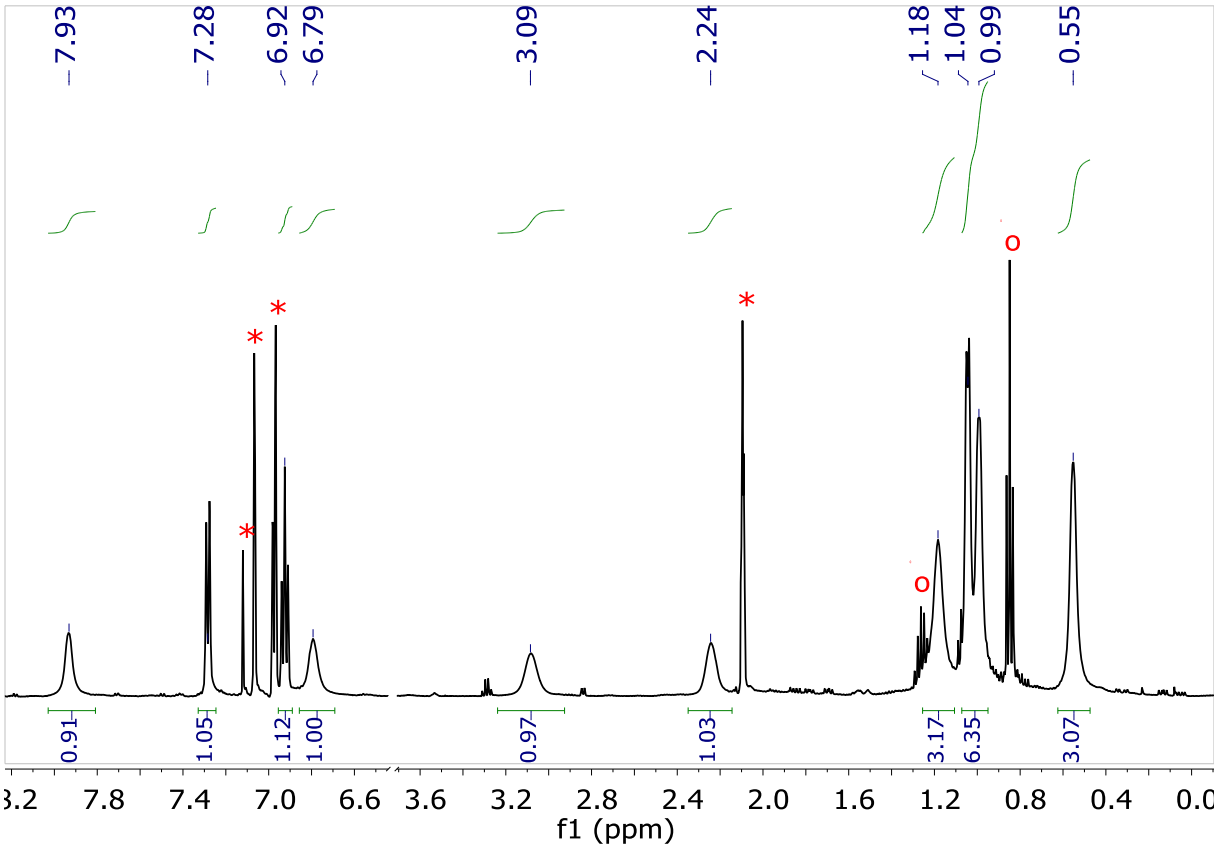


**Figure S13**. $^{1}$H NMR spectrum (500 MHz, 373 K) of **3-$N_2$** recorded in toluene-$d_8$. Peaks marked with an asterisk arise from toluene-$d_8$. Peaks marked with "o" correspond to adventitious pentane present in the NMR solvent. The smaller peaks scattered throughout the spectrum arise from the thermal decomposition of **3-$N_2$** and have not been assigned.

## Infrared Spectra

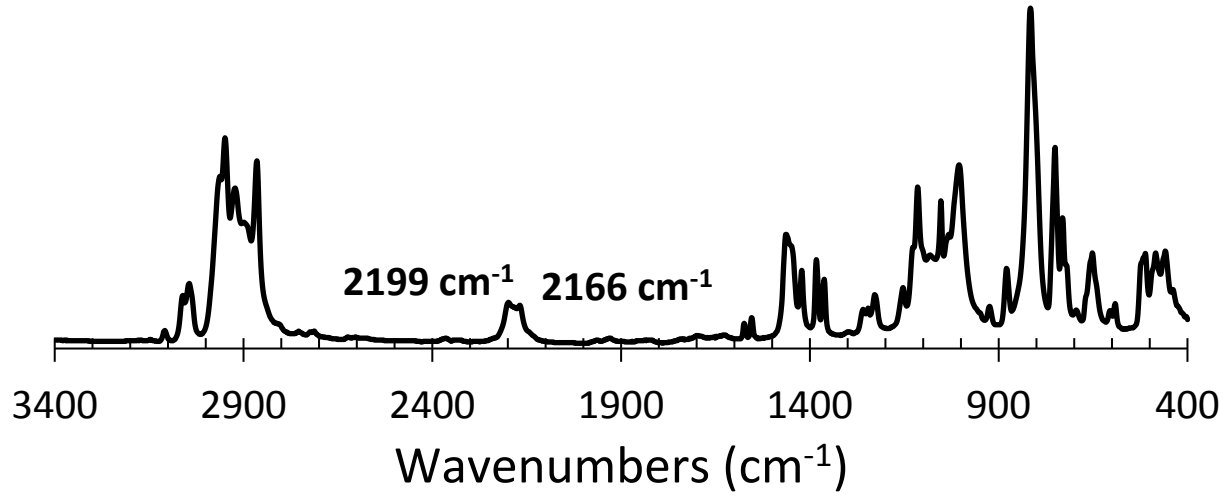


**Figure S14**. KBr-IR spectrum of solid **2.**

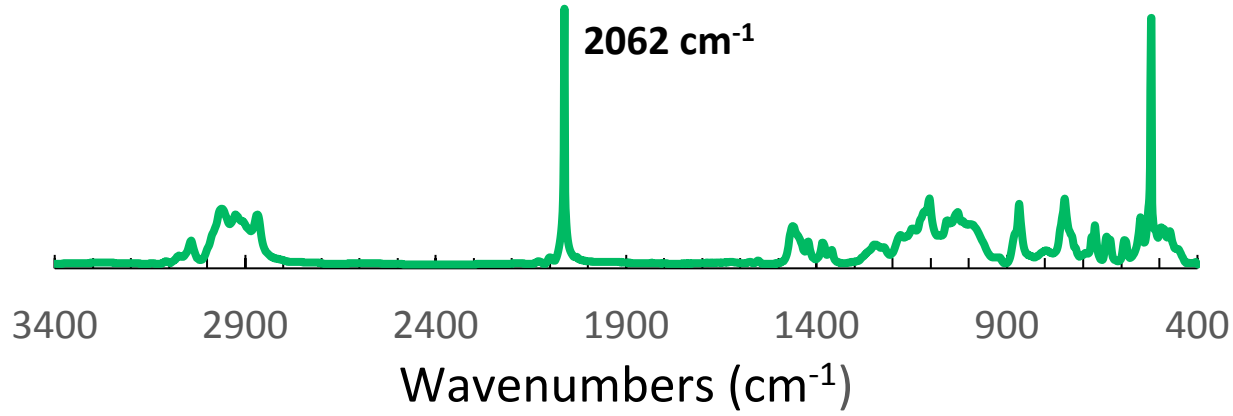


**Figure S15**. KBr-IR spectrum of solid **3-$N_2$**.

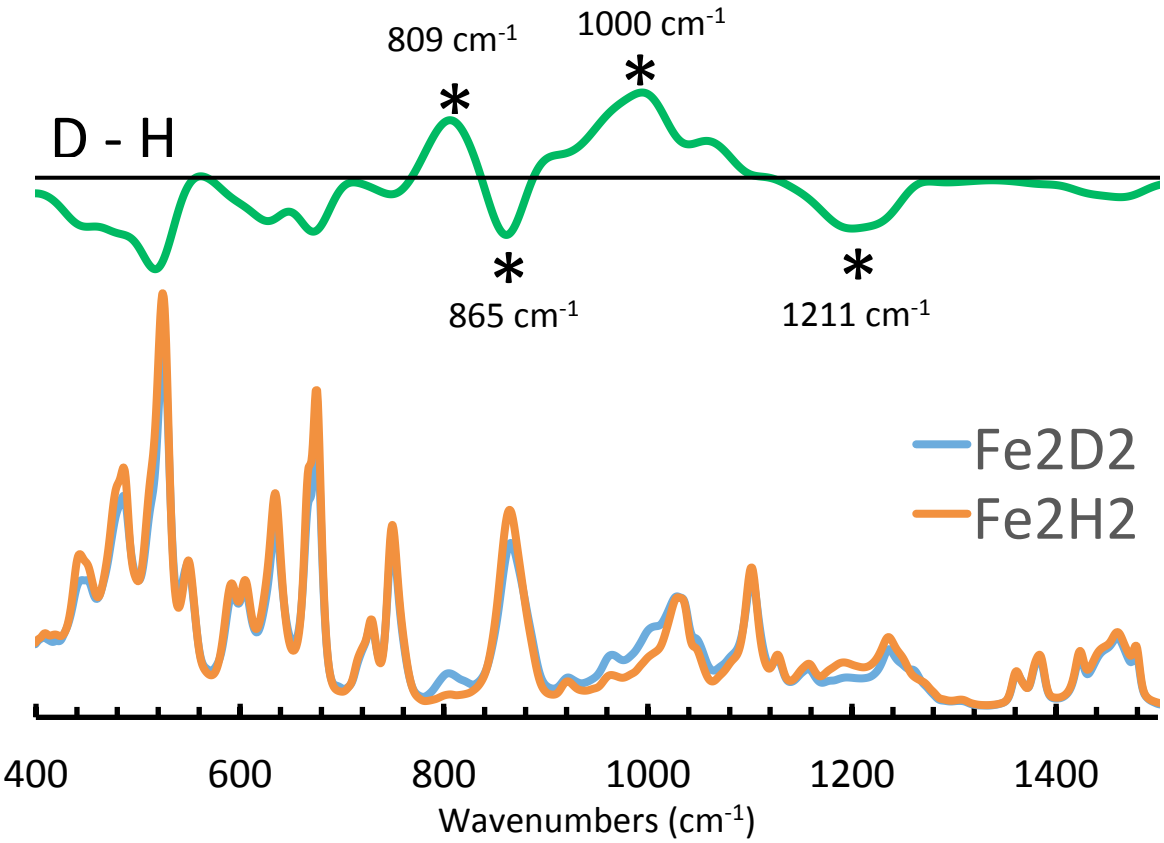


**Figure S16**. (Bottom) ATR-IR spectrum of **3-$N_2$** and **3-$N_2$-*$d_2$*** in a $C_6H_6$ thin film. (Top) smoothed difference spectrum obtained by subtracting the IR spectra of **3-$N_2$** from **3-$N_2$-*$d_2$***.

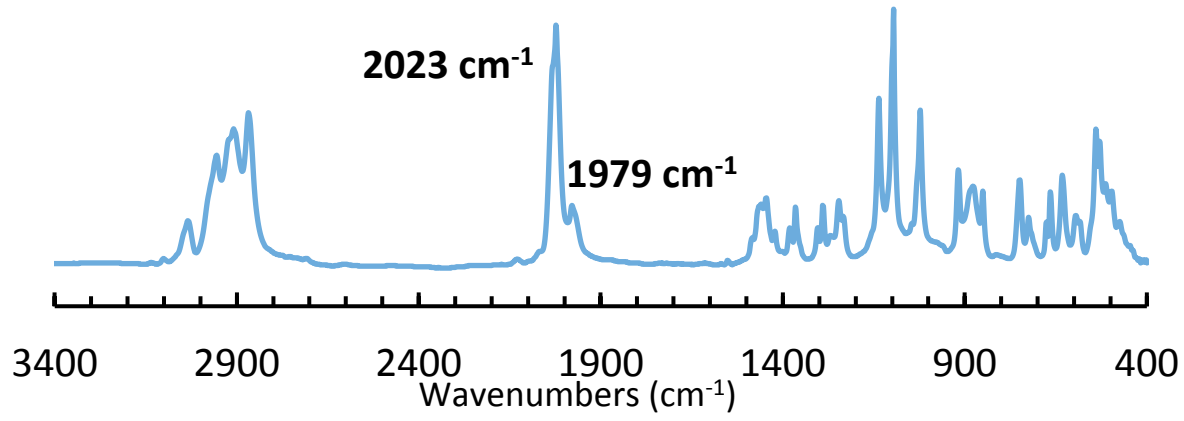


**Figure S17**. KBr IR spectrum of solid **4-$(N_2)_2$**.

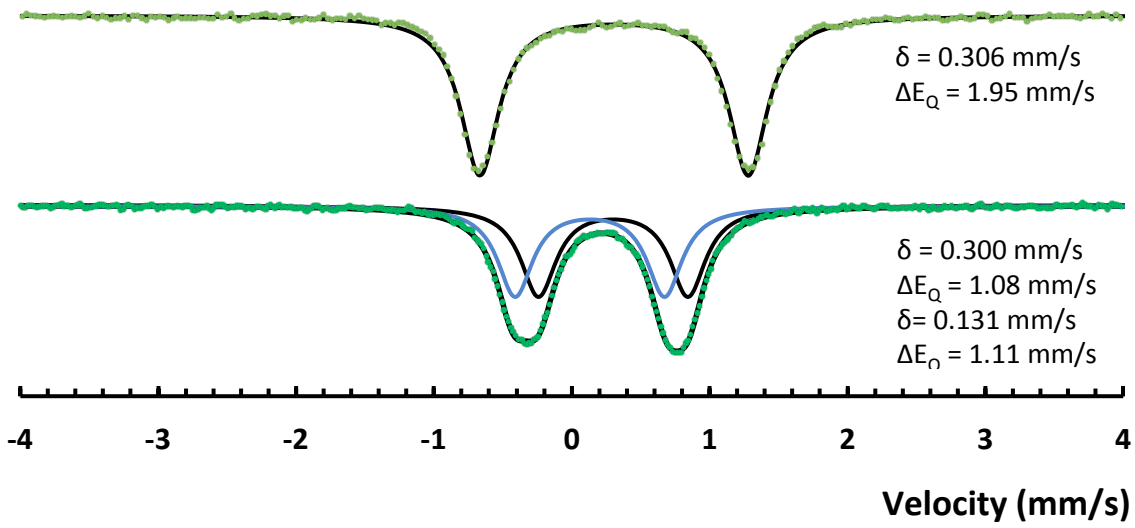


**Figure S18.** (Top) $^{57}$Fe Mossbauer spectrum of 5 mM $^{57}$**Fe-3-(N$_2$)$_2$** in a 2-MeTHF glass collected at 80 K. (Bottom) $^{57}$Fe Mossbauer spectrum of polycrystalline **3-N$_2$** collected at 80 K. Solid lines represent simulated spectra obtained from WMOSS. As each of the subspectra of polycrystalline **3-N$_2$** correspond to exactly 50% of the total absorption, a statistically-equivalent fit can be obtained with two species that display near-identical isomer shift values and very different quadrupole splittings. We have no data to favor one of these two sets of parameters and thus only show a representative simulation.

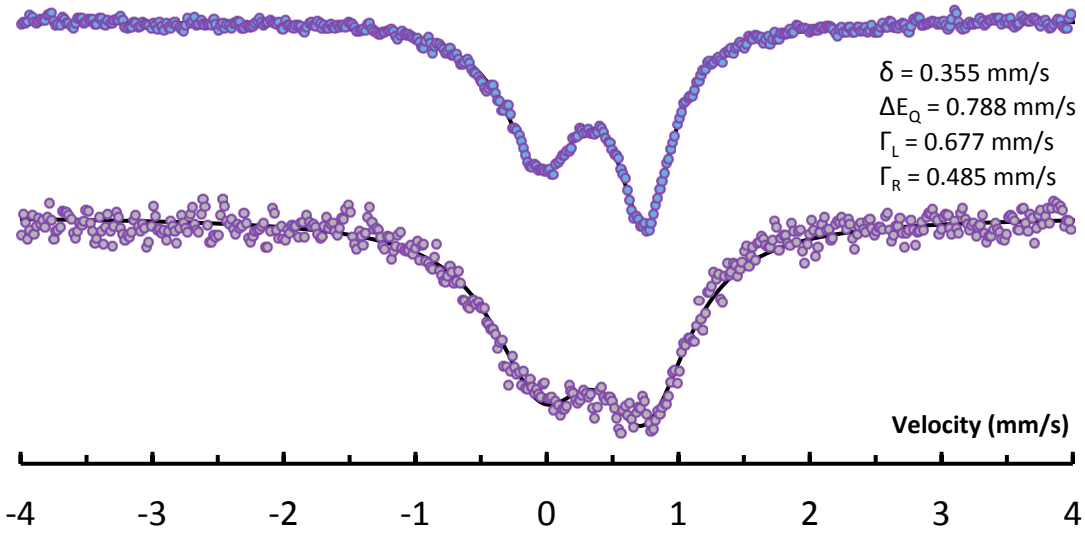


**Figure S19.** (Top) $^{57}$Fe Mossbauer spectrum of polycrystalline **4-(N$_2$)$_2$** collected at 80 K in the absence of a magnetic field. (Bottom) $^{57}$Fe Mossbauer spectrum of polycrystalline **4-(N$_2$)$_2$** collected at 80 K in the presence of a 50 mT field applied parallel to the direction of the gamma beam. The asymmetry of the quadrupole doublet and the dramatic line broadening observed upon application of a magnetic field to solid **4-(N$_2$)$_2$** can be explained by partially unquenched hyperfine coupling to the unpaired electron.

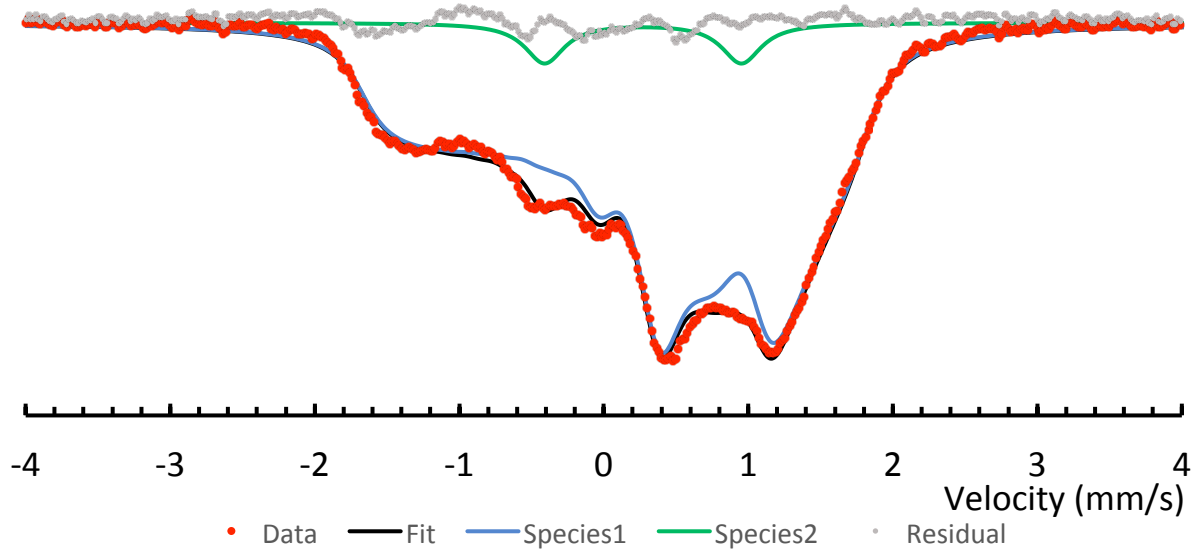


**Figure S20.** Full spectral simulation of $^{57}$Fe Mossbauer spectrum of 5mM **$^{57}$Fe-4-$(N_2)_2$** in a 2-MeTHF glass collected at 5 K with a 50 mT magnetic field applied parallel to the gamma beam. The data is shown in red dots and is fit to the sum of two species in a 94:6 ratio. The major species (blue) is attributed to **$^{57}$Fe-4-$(N_2)_2$** and the minor species (green) is an unknown impurity. The simulation parameters for the major species are listed in the main text. The minor species displays an isomer shift of 0.41 mm/s and a quadrupole splitting of 1.71 mm/s.

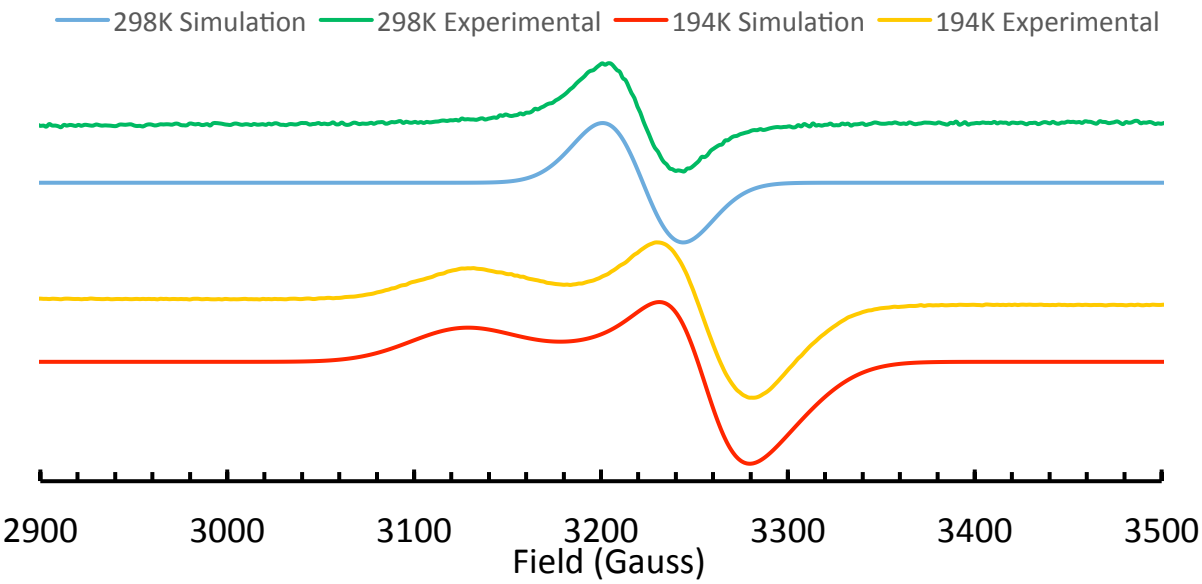


**Figure S21.** X-Band (9.376 GHz) EPR spectra of **4-$(N_2)_2$** in liquid 20:1 Toluene:THF solvent. (yellow) Spectrum collected at 194 K with 2 mW power and a modulation amplitude of 2 Gauss. (red) Simulation of yellow spectrum. Parameters derived from best fit: g = [2.1446, 2.05708, 2.03535] Hstrain = [198.5

113.5 182.5] (MHz). (green) Spectrum collected at 298 K with 2 mW power and a modulation amplitude of 2 Gauss. (blue) Simulation of green spectrum. Parameters derived from best fit: g = [2.0789] Hstrain = [147.5] (MHz).

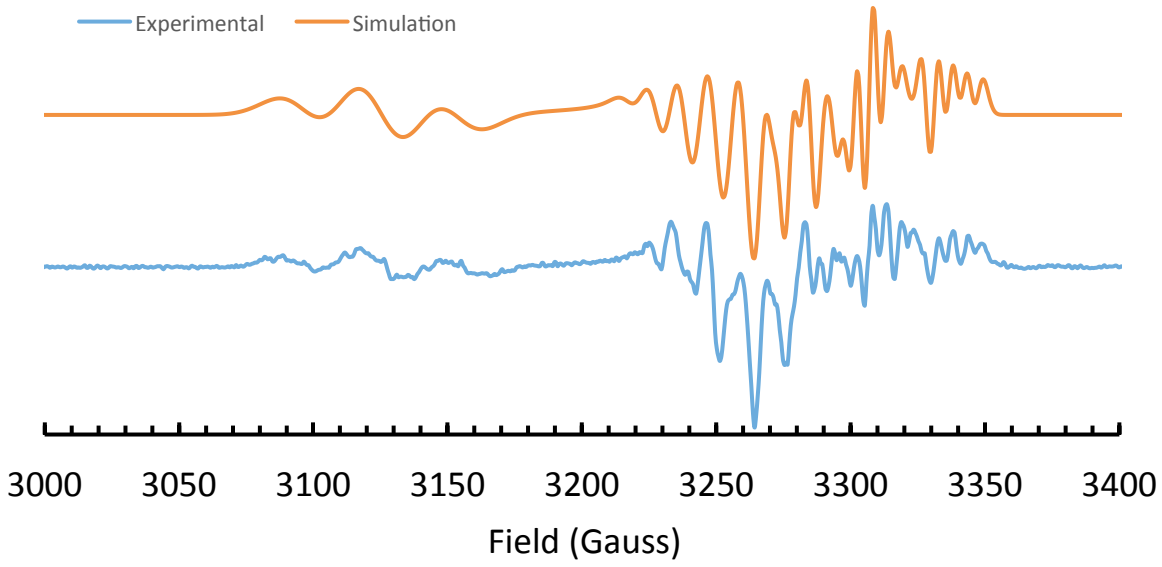


**Figure S22.** Second derivative of the EPR absorption envelope of **4-$(N_2)_2$** collected at 77 K in a 2-MeTHF glass. (Blue) Experimentally-obtained trace, (Orange) trace obtained from simulation.

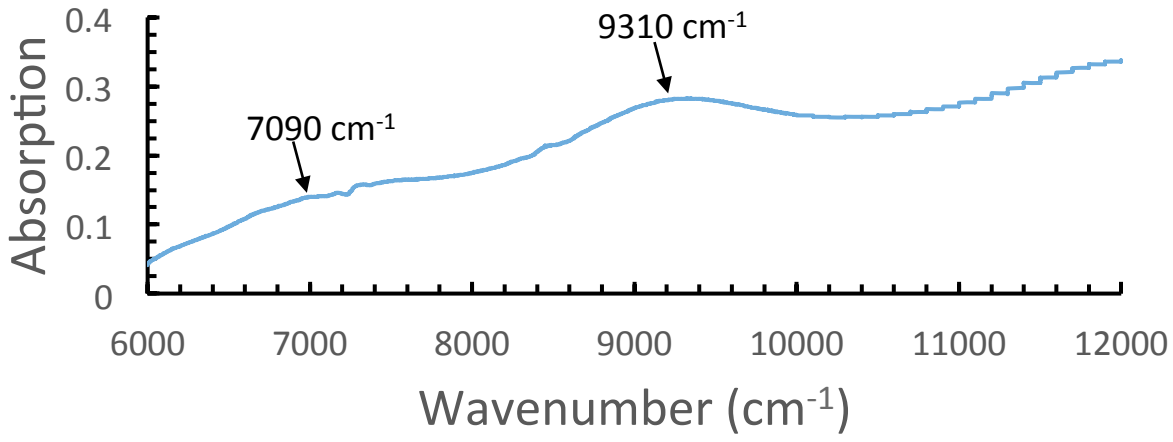


**Figure S23.** Near-Infrared Spectrum of **4-$(N_2)_2$** obtained as a 1 mM solution in 2-MeTHF.

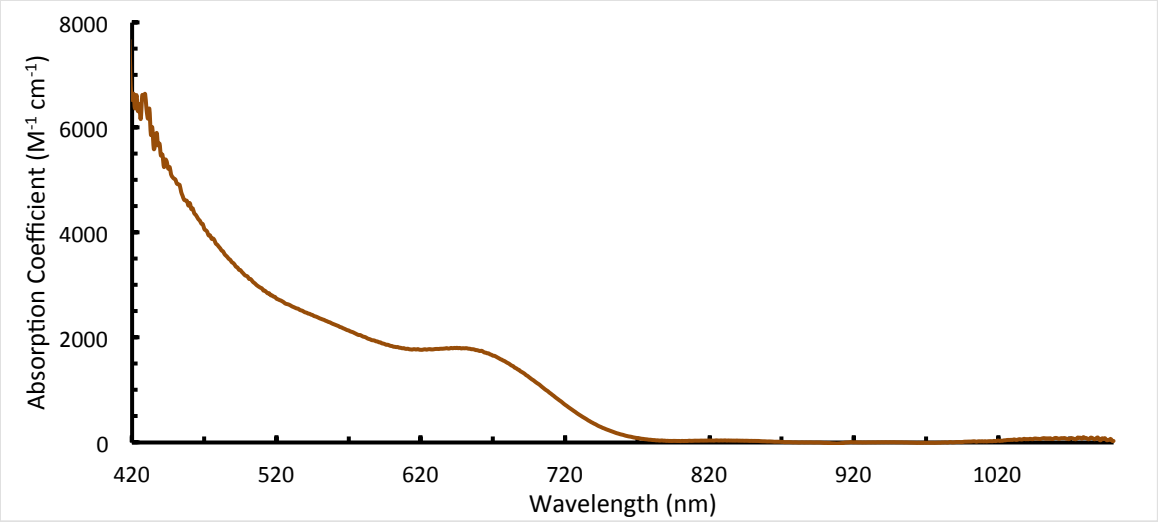


**Figure S24.** UV/visible Spectrum of **4-$(N_2)_2$** in 2-MeTHF.

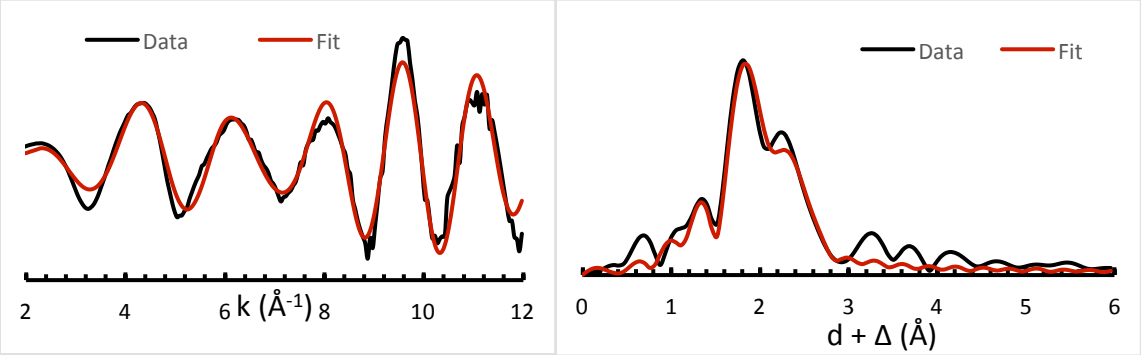


**Figure S25.** Extended X-Ray Absorption Fine Structure and Fourier transform of **3-$(N_2)_2$** prepared by dissolving **3-$N_2$** in 2-MeTHF (30 mM) and stirring at -100 °C for 5 minutes under an $N_2$ atmosphere, followed by rapid freezing at 77 K.

| Shell | Atomic # | N | R (Angstroms) | Debye-Waller | E0 |
|---|---|---|---|---|---|
| 1 | 26 | 1 | 2.7549 | 0.00197 | -4.144 |
| 2 | 15 | 3 | 2.2602 | 0.00285 | -4.144 |
| 3 | 7 | 1 | 1.8538 | 0.00314 | -4.144 |

**Table S1**. Best-fit parameters for EXAFS data on **3-$(N_2)_2$**. In shell 2, Si atoms were treated as P atoms.

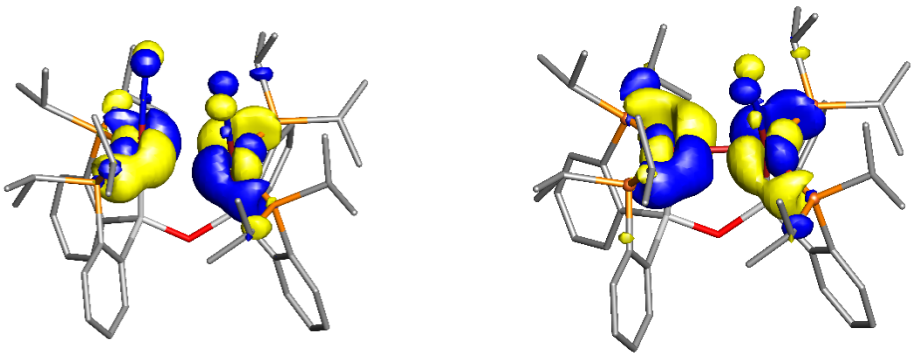

**Figure S26.** Singly Occupied Molecular Orbitals of (Left) **4-$N_2$** and (Right) **4-$(N_2)_2$**. Isosurface values drawn at 0.03.

# Variable Temperature $^1$H NMR Hydride Resonance

The chemical shift of the bridging hydride ligands in **3-$N_2$** can be fit with equation S1:

$$f(T) = A + (B*EXP(C/(8.3145*T)))/((1 + 3*EXP(C/(8.3145*T)))*T) \quad \text{(S1)}$$

Where A, B and C are constants derived from the fit and T is the temperature. A is the chemical shift (ppm) of the ground state of **3-$N_2$**, B is a fitting constant, and C is the difference in energy between the ground and excited states in Joules. The theoretical framework for the use of this equation is described in reference S1.

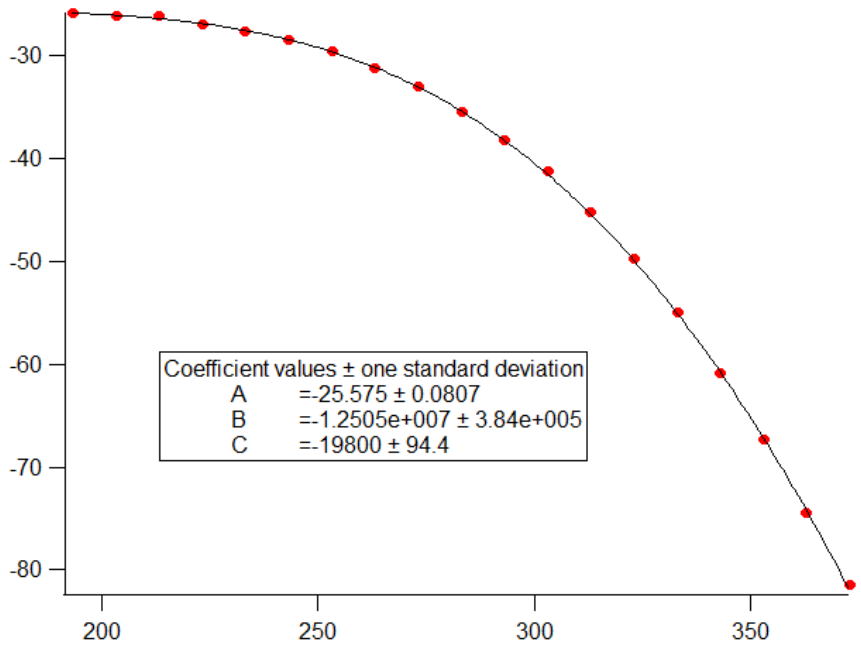


**Figure S27.** The temperature dependence of the $^1$H NMR chemical shift of the hydride resonance of **3-$N_2$** fit to equation S1. Resulting best fit parameters are listed in the legend.

| | | |
|---|---|---|
| Resistance[a] | 3500 Ohms | *Fixed |
| Double Layer Capacitance | 4 μFarad | *Fixed |
| Temperature | 298 K | *Fixed |
| Initial $[N_2]$[b] | 6 mM | *Fixed |
| Initial [**3-$N_2$**] | 1 mM | *Fixed |
| Redox Potential **3-$(N_2)_2$ / 4-$(N_2)_2$** | -2.0165 V | |
| Redox Potential **3-$N_2$ / 4-$N_2$** | -2.4008 V | |
| Alpha | 0.5 | *Fixed |
| ks | 10000 | *Fixed |
| ***3-$N_2$ + $N_2$ --> 3-$(N_2)_2$*** | | |
| $K_{eq}$ | 1.1 | *Fixed |
| Forward Rate constant | 520000 $M^{-1}s^{-1}$ | |
| ***4-$(N_2)_2$ --> 4-$N_2$ + $N_2$*** | | |
| $K_{eq}$ | 3.49E-07 | |
| Forward Rate Constant | 0.00405 $M^{-1}s^{-1}$ | |
| Diffusion Coefficient (Fe species) | 5.90E-06 | |
| Diffusion Coefficient ($N_2$) | 1.00E-05 | |

**Table S2**. Additional electrochemical parameters used in the simulation of the cyclic voltammograms.[a] The solution resistance was estimated for a typical system using a single-point high-frequency impedance measurements with a Bio-Logic VMP3 multichannel potentiostat/galvanostat with a built-in EIS analyzer. [b]The solubility of $N_2$ in tetrahydrofuran was taken from reference S3.

| compound | **3-$N_2$** | **4-$(N_2)_2$** |
|---|---|---|
| chem formula | $C_{48}H_{74}Fe_2N_2OP_4Si_2$ | $C_{70}H_{121}Fe_2N_4NaO_{10.5}P_4Si_4$ |
| fw | 986.85 | 1501.40 |
| cryst syst | Monoclinic | Triclinic |
| space group | P2(1)/n | P - 1 |
| a [Å] | 13.8412(19) | 14.5593(10) |
| b [Å] | 17.037(2) | 14.5601(10) |
| c [Å] | 20.983(3) | 21.2237(14) |
| α [°] | 90 | 94.695(2) |
| β [°] | 98.441(7) | 90.478(2) |
| γ [°] | 120 | 119.603(2) |
| V [$Å^3$] | 4894.5(11) | 3892.5(5) |
| Z | 4 | 2 |
| $D_{calcd}$ [g $cm^{-1}$] | 1.339 | 1.281 |
| F(000) | 2096 | 1608 |
| μ [$mm^{-1}$] | 0.810 | 0.548 |
| temp [K] | 100 | 100 |
| wavelength [Å] | 0.71073 | 0.71073 |

| | | |
|---|---|---|
| measurd reflns | 351417 | 144451 |
| unique reflns | 28246 | 24942 |
| data/restraints/param | 28246/0/556 | 23165/103/1195 |
| R(F) (I>2σ(I)) | 0.0345 | 0.0487 |
| wR($F^2$) (all) | 0.0846 | 0.1279 |
| GOF | 1.022 | 1.029 |

**Table S3**. X-Ray Diffraction table.

**3-$(N_2)_2$**

| # | Energy ($cm^{-1}$) | Reduced Mass | Force Constant | IR Intensity | Experimental Energy ($cm^{-1}$) |
|---|---|---|---|---|---|
| 325 | 1577.3304 | 5.1803 | 7.5937 | 0.0327 | |
| **326** | **2059.0038** | **13.678** | **34.1654** | **46.9248** | **2060** |
| **327** | **2089.1178** | **13.7805** | **35.4358** | **516.078** | **2097** |
| 328 | 2953.2754 | 1.0813 | 5.5564 | 11.9679 | |

**4-$(N_2)_2$**

| # | Energy ($cm^{-1}$) | Reduced Mass | Force Constant | IR Intensity | Experimental Energy ($cm^{-1}$) |
|---|---|---|---|---|---|
| 325 | 1573.8369 | 5.205 | 7.5961 | 0.0313 | |
| **326** | **2019.9581** | **13.7609** | **13.7609** | **70.0484** | **1979** |
| **327** | **2053.078** | **13.7258** | **13.7258** | **659.1349** | **2023** |
| 328 | 2942.726 | 1.0798 | 5.5094 | 12.1725 | |

**Table S4**. Calculated Vibrational Data (BP86, 6-31G(d))

# DFT Coordinates

**3-$N_2$** (S = 0)

| | | | |
|---|---|---|---|
| Fe | 1.24243800 | -0.16275400 | -0.77231800 |
| Fe | -1.22851800 | 0.15458400 | -0.65772900 |
| P | -2.70109300 | -1.49962900 | -0.88308800 |
| P | 2.53012500 | -1.98119500 | -0.38106800 |
| P | -2.53268500 | 1.94562200 | -0.55401000 |
| P | 2.78168300 | 1.53836200 | -0.80295800 |
| Si | -1.56501500 | -0.08933300 | 1.46210800 |
| Si | 1.29861600 | 0.15075600 | 1.47588200 |
| O | -0.13832600 | 0.05441900 | 2.38898300 |
| C | -2.24566200 | -1.83135800 | 1.82167900 |
| N | 0.95909300 | -0.35995500 | -2.52667000 |
| C | -1.73104200 | 3.66255100 | -0.74019200 |
| H | -2.54798600 | 4.37506500 | -0.51021500 |
| C | -2.77616300 | -2.50871600 | 0.69331900 |
| C | -2.78785000 | 1.21625300 | 2.12888000 |
| C | 1.75064000 | -3.69841200 | -0.60322100 |
| H | 2.53293600 | -4.39846500 | -0.24792500 |
| C | 1.98312000 | 1.88810900 | 1.83643400 |

| | | | |
|---|---|---|---|
| C | 4.17775700 | -2.17515900 | -1.35046400 |
| H | 4.82844900 | -1.42205900 | -0.87375900 |
| C | 2.65358000 | 2.53885400 | 0.77136500 |
| C | -3.34333000 | -3.79347400 | 0.85038500 |
| H | -3.76585300 | -4.33195000 | -0.00230900 |
| C | -4.03355500 | 2.12159900 | -1.74396800 |
| H | -4.74667600 | 1.38060800 | -1.34399600 |
| C | 3.00177400 | -2.12377900 | 1.42735000 |
| C | -4.56488500 | -1.28916500 | -1.24919300 |
| H | -4.57805600 | -0.53133400 | -2.05316600 |
| C | 4.67813800 | 1.29595500 | -0.88025200 |
| H | 4.80674300 | 0.54424500 | -1.68014300 |
| C | -2.04545400 | -2.61432200 | -2.29178600 |
| H | -0.95552500 | -2.50448200 | -2.14923400 |
| C | -2.25309700 | -2.47525500 | 3.07696700 |
| H | -1.80780600 | -1.97177300 | 3.94392800 |
| C | 2.45500700 | -1.13590200 | 2.28348900 |
| C | 1.85805800 | 2.54867400 | 3.07732500 |
| H | 1.30244100 | 2.06124500 | 3.88776400 |
| C | -3.23243700 | 2.16847900 | 1.17584100 |
| C | -3.22021400 | 1.33186000 | 3.46727700 |
| H | -2.87910500 | 0.60172200 | 4.21177300 |
| C | 0.52786500 | -3.86523900 | 0.30806500 |
| H | 0.13852800 | -4.89791100 | 0.23196500 |
| H | -0.28060200 | -3.17309600 | 0.02741000 |
| H | 0.77008500 | -3.67138100 | 1.36623500 |
| C | 3.22059300 | 3.81748500 | 0.97950800 |
| H | 3.74481200 | 4.34056400 | 0.17607300 |
| C | -5.27805700 | -0.72504600 | -0.00519300 |
| H | -6.30106800 | -0.39629100 | -0.27054900 |
| H | -4.74967900 | 0.13065300 | 0.44584700 |
| H | -5.36732400 | -1.50067700 | 0.77541600 |
| C | 4.91755200 | -3.52607800 | -1.26129100 |
| H | 5.83134900 | -3.47399500 | -1.88414600 |
| H | 4.31621900 | -4.36801700 | -1.64619900 |
| H | 5.24384700 | -3.76837300 | -0.23838000 |
| C | 2.40765900 | 3.82342100 | 3.27553400 |
| H | 2.30017300 | 4.32928700 | 4.24260900 |
| C | -2.34019200 | -4.12602900 | -2.27060600 |
| H | -1.79255500 | -4.60570100 | -3.10489600 |
| H | -3.40906100 | -4.36145000 | -2.40614600 |
| H | -1.99609200 | -4.59658000 | -1.33606800 |
| C | 2.35872000 | 2.65964700 | -2.29223500 |
| H | 1.26961400 | 2.48936200 | -2.35981100 |
| C | 3.09521600 | 4.45333000 | 2.22505100 |
| H | 3.52911400 | 5.44985800 | 2.36957700 |
| C | 3.76833800 | -3.17671500 | 1.97565700 |
| H | 4.14560700 | -3.98730200 | 1.34523100 |
| N | 0.70021700 | -0.47412600 | -3.64273500 |
| C | -0.62022400 | 3.86327000 | 0.29552100 |
| H | -0.22572400 | 4.89547500 | 0.23504600 |
| H | 0.21337400 | 3.16753300 | 0.11557200 |

| | | | |
|---|---|---|---|
| H | -0.97585900 | 3.69512100 | 1.32592200 |
| C | -3.35655600 | -4.41075500 | 2.11207400 |
| H | -3.79373200 | -5.41042200 | 2.22157200 |
| C | 5.18448200 | 0.71730300 | 0.45619700 |
| H | 6.22805300 | 0.36599200 | 0.34520400 |
| H | 4.57843100 | -0.12364600 | 0.82895100 |
| H | 5.17355700 | 1.49455000 | 1.24012100 |
| C | 4.00879100 | -1.77518600 | -2.83097600 |
| H | 5.00188700 | -1.73479300 | -3.31833500 |
| H | 3.53344700 | -0.78917800 | -2.94349700 |
| H | 3.39594200 | -2.49961300 | -3.39325900 |
| C | -2.80373200 | -3.75711200 | 3.22595600 |
| H | -2.80290600 | -4.24940100 | 4.20603200 |
| C | -4.07401800 | 2.37184800 | 3.86447100 |
| H | -4.40510900 | 2.44809500 | 4.90724200 |
| C | -4.77937300 | 3.46912500 | -1.80970900 |
| H | -5.59033800 | 3.39736500 | -2.56034400 |
| H | -4.12685000 | 4.30332700 | -2.12159700 |
| H | -5.25221000 | 3.73760500 | -0.85200700 |
| C | -4.06728700 | 3.23011300 | 1.58683700 |
| H | -4.37997200 | 4.00630700 | 0.88177900 |
| C | -2.37171100 | -1.98995400 | -3.66370400 |
| H | -1.88646200 | -2.58232900 | -4.46176900 |
| H | -1.98233200 | -0.96216900 | -3.75189300 |
| H | -3.45463900 | -1.97291400 | -3.87804600 |
| C | -5.35064800 | -2.51347100 | -1.75998800 |
| H | -6.40160400 | -2.21401900 | -1.94004500 |
| H | -5.37363000 | -3.32580800 | -1.01349500 |
| H | -4.96151900 | -2.91950000 | -2.70694200 |
| C | -3.63183700 | 1.66867900 | -3.16218200 |
| H | -4.53304400 | 1.54889300 | -3.79399700 |
| H | -3.09751400 | 0.70441600 | -3.14658600 |
| H | -2.97562300 | 2.40050400 | -3.66195700 |
| C | 2.72347500 | -1.20488000 | 3.66802400 |
| H | 2.29473400 | -0.44882800 | 4.33706100 |
| C | 2.56618400 | 4.18037200 | -2.17949100 |
| H | 2.15035500 | 4.66196500 | -3.08555700 |
| H | 3.63121800 | 4.46484300 | -2.12265000 |
| H | 2.04393000 | 4.60556100 | -1.30780200 |
| C | 3.51793200 | -2.22870800 | 4.20276400 |
| H | 3.72350200 | -2.26578200 | 5.27929900 |
| C | 1.43271500 | -4.03402500 | -2.07158100 |
| H | 0.81662500 | -4.95135000 | -2.12385900 |
| H | 2.34245900 | -4.21906200 | -2.66683300 |
| H | 0.87348700 | -3.22359200 | -2.56877600 |
| C | 4.03297200 | -3.22164600 | 3.35298200 |
| H | 4.63486900 | -4.04116500 | 3.76314200 |
| C | 2.97456100 | 2.10762400 | -3.59479800 |
| H | 2.53282100 | 2.63914900 | -4.45854500 |
| H | 2.76631600 | 1.03632300 | -3.73636700 |
| H | 4.06615300 | 2.25872000 | -3.64362300 |
| C | 5.54519800 | 2.51941800 | -1.24102000 |

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|---|---|---|---|
| H | 6.60365200 | 2.20026300 | -1.30325900 |
| H | 5.49180600 | 3.29713300 | -0.46024200 |
| H | 5.28424500 | 2.97726500 | -2.20752000 |
| C | -4.49155000 | 3.32558100 | 2.92205800 |
| H | -5.14511100 | 4.15173600 | 3.22653900 |
| C | -1.23340500 | 3.93723400 | -2.17026000 |
| H | -0.59166600 | 4.83834500 | -2.18384900 |
| H | -2.06027500 | 4.11384700 | -2.87820400 |
| H | -0.63611200 | 3.09396900 | -2.56124500 |
| H | 0.20133800 | 1.10915100 | -0.63806100 |
| H | -0.07216200 | -1.01173500 | -0.23342300 |

**3-$(N_2)_2$** (S = 0)

| | | | |
|---|---|---|---|
| Fe | -1.35335900 | 0.17417300 | -0.76989300 |
| Fe | 1.35349400 | -0.17395600 | -0.76978400 |
| P | 2.75430200 | 1.62103200 | -0.84056300 |
| P | -2.68504900 | 1.93392000 | -0.31798600 |
| P | 2.68510700 | -1.93386500 | -0.31766500 |
| P | -2.75377100 | -1.62125500 | -0.84103600 |
| Si | 1.43843600 | 0.17939200 | 1.46822300 |
| Si | -1.43875400 | -0.17924000 | 1.46820800 |
| O | -0.00020800 | 0.00011900 | 2.35407400 |
| C | 2.01039000 | 1.96263400 | 1.80832800 |
| N | -1.28007100 | 0.54102200 | -2.52948200 |
| C | 1.95027600 | -3.66941600 | -0.55444100 |
| H | 2.74982400 | -4.35071100 | -0.20104800 |
| C | 2.59202800 | 2.64633300 | 0.71259000 |
| C | 2.64407100 | -1.02816500 | 2.31989700 |
| C | -1.95004200 | 3.66947200 | -0.55386600 |
| H | -2.74978500 | 4.35065000 | -0.20067600 |
| C | -2.01095500 | -1.96240700 | 1.80828900 |
| C | -4.37360200 | 2.07642800 | -1.23520400 |
| H | -4.97565600 | 1.29600700 | -0.73767400 |
| C | -2.59284600 | -2.64590100 | 0.71258000 |
| C | 3.06851400 | 3.96684000 | 0.88198500 |
| H | 3.52174700 | 4.51525000 | 0.05254500 |
| C | 4.37415800 | -2.07613100 | -1.23392500 |
| H | 4.97588700 | -1.29554200 | -0.73625700 |
| C | -3.15662200 | 2.05550700 | 1.49084600 |
| C | 4.65856400 | 1.49830000 | -0.94963100 |
| H | 4.82286200 | 0.73228700 | -1.72823500 |
| C | -4.65793000 | -1.49852800 | -0.95254100 |
| H | -4.82113300 | -0.73227700 | -1.73113900 |
| C | 2.19836000 | 2.66207700 | -2.34566200 |
| H | 1.12757000 | 2.38919700 | -2.39714700 |
| C | 1.87861000 | 2.63166700 | 3.04418600 |
| H | 1.38932800 | 2.11962400 | 3.88178800 |
| C | -2.64504500 | 1.02786600 | 2.31954700 |
| C | -1.87968800 | -2.63142600 | 3.04421400 |
| H | -1.39018600 | -2.11961500 | 3.88183100 |

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|---|---|---|---|
| C | 3.15564400 | -2.05593400 | 1.49139700 |
| C | 2.94264900 | -1.04658100 | 3.69961500 |
| H | 2.54696200 | -0.25515900 | 4.34791400 |
| C | -0.72430700 | 3.86206900 | 0.34661500 |
| H | -0.36133800 | 4.90451900 | 0.27178800 |
| H | 0.09482900 | 3.19251900 | 0.04105100 |
| H | -0.94365100 | 3.65467000 | 1.40703900 |
| C | -3.07022000 | -3.96609500 | 0.88205600 |
| H | -3.52369700 | -4.51424000 | 0.05257200 |
| C | 5.21840300 | 0.98896200 | 0.39365100 |
| H | 6.27650400 | 0.68874700 | 0.27275700 |
| H | 4.66149600 | 0.12884700 | 0.79964900 |
| H | 5.18004700 | 1.78716900 | 1.15502600 |
| C | -5.14537300 | 3.40492700 | -1.08987100 |
| H | -6.08777400 | 3.33485000 | -1.66656000 |
| H | -4.58503900 | 4.26525100 | -1.49653500 |
| H | -5.42486800 | 3.62704000 | -0.04917500 |
| C | -2.34177400 | -3.94550500 | 3.20637100 |
| H | -2.23240400 | -4.45635800 | 4.17063400 |
| C | 2.27342600 | 4.19749900 | -2.25889100 |
| H | 1.79835400 | 4.62585700 | -3.16218700 |
| H | 3.31242500 | 4.57000500 | -2.23141300 |
| H | 1.73711000 | 4.59226400 | -1.38167900 |
| C | -2.19596100 | -2.66297900 | -2.34496600 |
| H | -1.12492900 | -2.39077500 | -2.39475300 |
| C | -2.94318700 | -4.60893800 | 2.12385300 |
| H | -3.30736200 | -5.63648700 | 2.24082600 |
| C | -3.90371400 | 3.10935400 | 2.06363600 |
| H | -4.24371600 | 3.95506500 | 1.45870600 |
| N | -1.20989600 | 0.87730100 | -3.62391700 |
| C | 0.72408000 | -3.86213400 | 0.34544900 |
| H | 0.36123800 | -4.90460300 | 0.27046700 |
| H | -0.09488100 | -3.19257800 | 0.03943100 |
| H | 0.94288500 | -3.65466900 | 1.40596200 |
| C | 2.94090500 | 4.60974900 | 2.12370400 |
| H | 3.30437800 | 5.63755900 | 2.24057200 |
| C | -5.21937200 | -0.98952000 | 0.39022500 |
| H | -6.27723100 | -0.68896900 | 0.26807400 |
| H | -4.66274300 | -0.12973100 | 0.79731700 |
| H | -5.18221500 | -1.78805600 | 1.15132000 |
| C | -4.28020900 | 1.71147800 | -2.73091700 |
| H | -5.30049700 | 1.66860900 | -3.15800900 |
| H | -3.80092700 | 0.73736800 | -2.90324200 |
| H | -3.71165800 | 2.45738000 | -3.31084600 |
| C | 2.33986000 | 3.94605600 | 3.20625900 |
| H | 2.23009500 | 4.45694700 | 4.17045600 |
| C | 3.72302400 | -2.06909600 | 4.25732600 |
| H | 3.95151200 | -2.06939300 | 5.32989300 |
| C | 5.14614300 | -3.40445600 | -1.08803500 |
| H | 6.08904500 | -3.33404100 | -1.66383900 |
| H | 4.58630900 | -4.26482700 | -1.49531800 |
| H | 5.42461900 | -3.62668400 | -0.04708600 |

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|---|---|---|---|
| C | 3.90203200 | -3.11013400 | 2.06443500 |
| H | 4.24204400 | -3.95592600 | 1.45959400 |
| C | 2.85049900 | 2.15296100 | -3.64834200 |
| H | 2.32658700 | 2.60031900 | -4.51322300 |
| H | 2.77956100 | 1.06127600 | -3.76089400 |
| H | 3.91249300 | 2.44117300 | -3.72336000 |
| C | 5.43066100 | 2.76975500 | -1.35584800 |
| H | 6.50781000 | 2.52584400 | -1.43368300 |
| H | 5.33483900 | 3.55796200 | -0.59002200 |
| H | 5.11751700 | 3.18637600 | -2.32547100 |
| C | 4.28118100 | -1.71140900 | -2.72971700 |
| H | 5.30154300 | -1.66857600 | -3.15660500 |
| H | 3.80191600 | -0.73731800 | -2.90228300 |
| H | 3.71272800 | -2.45740900 | -3.30960300 |
| C | -2.94426500 | 1.04610400 | 3.69911800 |
| H | -2.54860500 | 0.25478200 | 4.34755700 |
| C | -2.27221500 | -4.19833300 | -2.25787900 |
| H | -1.79634600 | -4.62727800 | -3.16047800 |
| H | -3.31155000 | -4.57001300 | -2.23161300 |
| H | -1.73733100 | -4.59337700 | -1.37992400 |
| C | -3.72532000 | 2.06825600 | 4.25653500 |
| H | -3.95430500 | 2.06837800 | 5.32899600 |
| C | -1.62785500 | 4.01399400 | -2.01688200 |
| H | -1.15470100 | 5.01298700 | -2.06664100 |
| H | -2.52563900 | 4.04142400 | -2.65570700 |
| H | -0.92749700 | 3.28669700 | -2.45946500 |
| C | -4.19214400 | 3.10949000 | 3.43699800 |
| H | -4.77638100 | 3.93097700 | 3.86813900 |
| C | -2.84560300 | -2.15391500 | -3.64889900 |
| H | -2.32060100 | -2.60203700 | -4.51272600 |
| H | -2.77367500 | -1.06234000 | -3.76180800 |
| H | -3.90768100 | -2.44137300 | -3.72555600 |
| C | -5.42990000 | -2.76963500 | -1.36012000 |
| H | -6.50683400 | -2.52524600 | -1.43941100 |
| H | -5.33556600 | -3.55813900 | -0.59440300 |
| H | -5.11558500 | -3.18612100 | -2.32941900 |
| C | 4.18979500 | -3.11047900 | 3.43794100 |
| H | 4.77348100 | -3.93224100 | 3.86930600 |
| C | 1.62876400 | -4.01357500 | -2.01770700 |
| H | 1.15458400 | -5.01206200 | -2.06783300 |
| H | 2.52701100 | -4.04197000 | -2.65586200 |
| H | 0.92951200 | -3.28558900 | -2.46088800 |
| H | -0.13305700 | -0.96945500 | -0.41823200 |
| H | 0.13388900 | 0.97023600 | -0.41897700 |
| N | 1.28087700 | -0.54026800 | -2.52966900 |
| N | 1.21150800 | -0.87572200 | -3.62441900 |

**3-$N_2$** (S = 1)

| | | | |
|---|---|---|---|
| Fe | 1.33652200 | -0.23913700 | -0.80364600 |
| Fe | -1.18651200 | 0.22640800 | -0.75464600 |

| | | | |
|---|---|---|---|
| P | -2.60864900 | -1.59405900 | -1.06748700 |
| P | 2.56273000 | -2.02801900 | -0.13700800 |
| P | -2.40399200 | 2.15882700 | -0.47496500 |
| P | 2.78398700 | 1.51737900 | -0.83861400 |
| Si | -1.72622500 | -0.09932900 | 1.37556800 |
| Si | 1.18065700 | 0.24219200 | 1.40792600 |
| O | -0.31510500 | 0.14671100 | 2.27398800 |
| C | -2.34773000 | -1.87439500 | 1.66888300 |
| N | 1.26672400 | -0.65659100 | -2.53522100 |
| C | -1.72765100 | 3.92995800 | -0.41854300 |
| H | -2.61896600 | 4.58863300 | -0.44328400 |
| C | -2.80480300 | -2.56088600 | 0.51341000 |
| C | -3.07432500 | 1.10839300 | 1.99147700 |
| C | 1.84367900 | -3.77744000 | -0.31484200 |
| H | 2.59062200 | -4.44521000 | 0.15865900 |
| C | 1.79599000 | 2.02069800 | 1.71032300 |
| C | 4.31946300 | -2.24504900 | -0.89508000 |
| H | 4.88434000 | -1.43307300 | -0.40437500 |
| C | 2.48172900 | 2.64005200 | 0.63209100 |
| C | -3.37774500 | -3.84593700 | 0.64078700 |
| H | -3.74700400 | -4.38623300 | -0.23528400 |
| C | -3.65367000 | 2.23896400 | -1.92070600 |
| H | -4.39241500 | 1.46923600 | -1.63673400 |
| C | 2.85348900 | -2.03647000 | 1.71462100 |
| C | -4.41937700 | -1.33781300 | -1.61575600 |
| H | -4.33866200 | -0.58766400 | -2.42672400 |
| C | 4.68539300 | 1.32389000 | -0.67264400 |
| H | 4.91757000 | 0.51235000 | -1.38703500 |
| C | -1.82870100 | -2.72096400 | -2.39180400 |
| H | -0.75685200 | -2.60339600 | -2.14814400 |
| C | -2.42804900 | -2.51422500 | 2.92427100 |
| H | -2.03879300 | -2.00726700 | 3.81586600 |
| C | 2.26617600 | -0.96073300 | 2.42482500 |
| C | 1.62322600 | 2.73323200 | 2.91696500 |
| H | 1.06693600 | 2.26566500 | 3.73887500 |
| C | -3.41194000 | 2.14969500 | 1.08975400 |
| C | -3.74844400 | 1.03587900 | 3.22912000 |
| H | -3.50590600 | 0.23225200 | 3.93502700 |
| C | 0.53665400 | -3.89674400 | 0.47951400 |
| H | 0.14470800 | -4.92974700 | 0.41688100 |
| H | -0.23207500 | -3.21321300 | 0.08643200 |
| H | 0.67652900 | -3.64952600 | 1.54502600 |
| C | 2.97994700 | 3.95404800 | 0.78859400 |
| H | 3.50798900 | 4.45718600 | -0.02544500 |
| C | -5.22141300 | -0.72951300 | -0.45029300 |
| H | -6.20876400 | -0.38142900 | -0.80847800 |
| H | -4.70653800 | 0.12102400 | 0.02496000 |
| H | -5.39543800 | -1.48456000 | 0.33646400 |
| C | 5.07176400 | -3.55907700 | -0.60429600 |
| H | 6.05929000 | -3.52705800 | -1.10388800 |
| H | 4.54330800 | -4.44614000 | -0.99643800 |
| H | 5.25989600 | -3.71063500 | 0.46970800 |

| | | | |
|---|---|---|---|
| C | 2.11836900 | 4.03708200 | 3.06587300 |
| H | 1.97392500 | 4.58149500 | 4.00695200 |
| C | -2.13090300 | -4.22986800 | -2.39517300 |
| H | -1.52136700 | -4.71423500 | -3.18208200 |
| H | -3.18783700 | -4.45662500 | -2.61500200 |
| H | -1.86429500 | -4.70257000 | -1.43653500 |
| C | 2.54077500 | 2.49696800 | -2.46655400 |
| H | 1.46579300 | 2.31283900 | -2.65420700 |
| C | 2.79487300 | 4.64659700 | 1.99666500 |
| H | 3.18015400 | 5.66817000 | 2.09903600 |
| C | 3.53692600 | -3.05065800 | 2.42289600 |
| H | 3.93760500 | -3.92724400 | 1.90457600 |
| N | 1.12515800 | -0.90686900 | -3.65045500 |
| C | -0.97022800 | 4.18766800 | 0.89160600 |
| H | -0.57611600 | 5.22109500 | 0.89990500 |
| H | -0.11619600 | 3.50148900 | 1.00117500 |
| H | -1.61958800 | 4.06345300 | 1.77388700 |
| C | -3.46921300 | -4.45618700 | 1.90236300 |
| H | -3.91322200 | -5.45470900 | 1.99055000 |
| C | 5.03465800 | 0.85441700 | 0.75286200 |
| H | 6.08284100 | 0.50085100 | 0.78947100 |
| H | 4.38604100 | 0.03977800 | 1.11203300 |
| H | 4.93756200 | 1.68739200 | 1.47083700 |
| C | 4.32697200 | -1.96682200 | -2.41146600 |
| H | 5.37166900 | -1.94275600 | -2.77709100 |
| H | 3.85820200 | -1.00288100 | -2.65972100 |
| H | 3.79602800 | -2.74584400 | -2.98422300 |
| C | -2.98321800 | -3.79752000 | 3.04384400 |
| H | -3.03913900 | -4.28549200 | 4.02422400 |
| C | -4.73385300 | 1.97608400 | 3.56940100 |
| H | -5.25383900 | 1.90443000 | 4.53211900 |
| C | -4.41064400 | 3.55988000 | -2.14359200 |
| H | -5.12887100 | 3.43374500 | -2.97674600 |
| H | -3.73441000 | 4.38750200 | -2.42110900 |
| H | -4.99100400 | 3.86851800 | -1.25863100 |
| C | -4.38542500 | 3.10714300 | 1.44344200 |
| H | -4.62425600 | 3.93940400 | 0.77236500 |
| C | -2.03047900 | -2.09342500 | -3.78647100 |
| H | -1.42563700 | -2.64518700 | -4.52862700 |
| H | -1.68802600 | -1.04530900 | -3.81989100 |
| H | -3.08269800 | -2.12747800 | -4.12037200 |
| C | -5.18629500 | -2.55207800 | -2.17515100 |
| H | -6.20513600 | -2.23157700 | -2.46761000 |
| H | -5.30552600 | -3.34192100 | -1.41307800 |
| H | -4.71456300 | -2.99562100 | -3.06601700 |
| C | -2.96646000 | 1.77679600 | -3.22308400 |
| H | -3.71117500 | 1.64927100 | -4.03198600 |
| H | -2.44989500 | 0.80725700 | -3.09193800 |
| H | -2.21256000 | 2.50124500 | -3.57484400 |
| C | 2.41872700 | -0.90200400 | 3.82744600 |
| H | 1.95881600 | -0.07707500 | 4.38516200 |
| C | 2.75694000 | 4.02130600 | -2.48722600 |

| | | | |
|---|---|---|---|
| H | 2.47289600 | 4.41003700 | -3.48462900 |
| H | 3.81000300 | 4.30413100 | -2.31746100 |
| H | 2.13405700 | 4.53995200 | -1.74159900 |
| C | 3.13455700 | -1.88772500 | 4.52157500 |
| H | 3.24992000 | -1.82499600 | 5.61048800 |
| C | 1.66970400 | -4.21295000 | -1.78016700 |
| H | 1.10464000 | -5.16333400 | -1.82777500 |
| H | 2.63668200 | -4.38095500 | -2.28299700 |
| H | 1.11887700 | -3.46066800 | -2.36945700 |
| C | 3.68345600 | -2.97152500 | 3.81628000 |
| H | 4.22049900 | -3.76331600 | 4.35203700 |
| C | 3.30802400 | 1.81507700 | -3.61932300 |
| H | 3.00026600 | 2.26658600 | -4.58140200 |
| H | 3.09085600 | 0.73807300 | -3.68327100 |
| H | 4.40007900 | 1.94562400 | -3.53200600 |
| C | 5.57303300 | 2.53467800 | -1.01905500 |
| H | 6.63601300 | 2.25124800 | -0.89091700 |
| H | 5.38205000 | 3.37950100 | -0.33530600 |
| H | 5.45297200 | 2.88936800 | -2.05458200 |
| C | -5.05048800 | 3.01337600 | 2.67660400 |
| H | -5.81427200 | 3.75387500 | 2.94164000 |
| C | -0.85095100 | 4.22924300 | -1.64199400 |
| H | -0.40722900 | 5.23869500 | -1.55404300 |
| H | -1.41480900 | 4.19726000 | -2.58990000 |
| H | -0.02601000 | 3.49984600 | -1.71176000 |
| H | 0.33088000 | 1.02279600 | -1.05234000 |
| H | -0.02230800 | -1.03354200 | -0.39740100 |

**4-$N_2$** (S = 1/2)

| | | | |
|---|---|---|---|
| Fe | 1.33526600 | -0.18401000 | -0.83172100 |
| Fe | -1.26886100 | 0.16926300 | -0.68922000 |
| P | -2.60491800 | -1.56292400 | -0.93606700 |
| P | 2.59486500 | -1.96120800 | -0.31219600 |
| P | -2.55659700 | 1.94313900 | -0.54774200 |
| P | 2.72864500 | 1.60503300 | -0.81865700 |
| Si | -1.61206200 | -0.13769200 | 1.40772100 |
| Si | 1.24476900 | 0.18092800 | 1.40594100 |
| O | -0.18450100 | 0.02307700 | 2.34198400 |
| C | -2.25018200 | -1.90873400 | 1.77678900 |
| N | 1.15816700 | -0.47259600 | -2.57277000 |
| C | -1.87358100 | 3.72845100 | -0.65206100 |
| H | -2.71876400 | 4.40717700 | -0.41824100 |
| C | -2.71715000 | -2.60397400 | 0.62971900 |
| C | -2.89073700 | 1.11564100 | 2.10751500 |
| C | 1.91678300 | -3.73227800 | -0.50612100 |
| H | 2.70029000 | -4.41041300 | -0.11092800 |
| C | 1.85855000 | 1.95228900 | 1.79412600 |
| C | 4.31397500 | -2.13285700 | -1.18691500 |
| H | 4.90382900 | -1.33745300 | -0.69770600 |

| | | | |
|---|---|---|---|
| C | 2.53778900 | 2.62564600 | 0.74729500 |
| C | -3.23705700 | -3.91055700 | 0.76771100 |
| H | -3.61000400 | -4.46101100 | -0.10129000 |
| C | -4.06644300 | 2.09649400 | -1.75299700 |
| H | -4.73712900 | 1.29979900 | -1.38607800 |
| C | 3.02486400 | -2.04334100 | 1.51868100 |
| C | -4.47999100 | -1.42624000 | -1.35278100 |
| H | -4.49449700 | -0.65722100 | -2.14884600 |
| C | 4.64675600 | 1.46122800 | -0.83872300 |
| H | 4.82162000 | 0.69340600 | -1.61493300 |
| C | -1.90518200 | -2.67570700 | -2.33631800 |
| H | -0.82166900 | -2.54016900 | -2.16590900 |
| C | -2.27765300 | -2.55791100 | 3.02946800 |
| H | -1.88023800 | -2.04113600 | 3.91262600 |
| C | 2.44004900 | -1.02462900 | 2.31288200 |
| C | 1.67808600 | 2.61032600 | 3.03010200 |
| H | 1.11116000 | 2.10489700 | 3.82225000 |
| C | -3.32981100 | 2.09323600 | 1.17439300 |
| C | -3.37665700 | 1.16786500 | 3.43160300 |
| H | -3.04240700 | 0.41702000 | 4.15952700 |
| C | 0.65839500 | -3.90252200 | 0.35579500 |
| H | 0.27582000 | -4.93914600 | 0.27967500 |
| H | -0.14041300 | -3.21698000 | 0.03134600 |
| H | 0.85482200 | -3.68894300 | 1.41990200 |
| C | 3.05148700 | 3.92375300 | 0.97189100 |
| H | 3.57747800 | 4.46494100 | 0.18049100 |
| C | -5.23727600 | -0.88623100 | -0.12531200 |
| H | -6.26395100 | -0.57893600 | -0.40810500 |
| H | -4.73426200 | -0.02118700 | 0.33752300 |
| H | -5.32195400 | -1.66660200 | 0.65199300 |
| C | 5.10270300 | -3.44726100 | -1.01694500 |
| H | 6.05160700 | -3.38441000 | -1.58741700 |
| H | 4.55254400 | -4.32287700 | -1.40634400 |
| H | 5.37202500 | -3.64645500 | 0.03203400 |
| C | 2.17982600 | 3.90264000 | 3.24518300 |
| H | 2.02733800 | 4.40469900 | 4.20953100 |
| C | -2.16378200 | -4.19353600 | -2.34914200 |
| H | -1.58883300 | -4.65211000 | -3.17888300 |
| H | -3.22537600 | -4.45185100 | -2.50695600 |
| H | -1.82750300 | -4.66973800 | -1.41388700 |
| C | 2.32077400 | 2.73003100 | -2.31643500 |
| H | 1.23727700 | 2.52619300 | -2.40079900 |
| C | 2.87370200 | 4.55666100 | 2.21352600 |
| H | 3.26887200 | 5.56882900 | 2.36886900 |
| C | 3.79237700 | -3.05589400 | 2.13726100 |
| H | 4.19194400 | -3.89261300 | 1.55457800 |
| N | 0.95216600 | -0.64884500 | -3.69716000 |
| C | -0.78508800 | 3.92738000 | 0.40738100 |
| H | -0.40010600 | 4.96606300 | 0.38071400 |
| H | 0.06045400 | 3.24471100 | 0.22971100 |
| H | -1.15825100 | 3.72727000 | 1.42597000 |
| C | -3.26824300 | -4.53498000 | 2.02669400 |

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|---|---|---|---|
| H | -3.66682500 | -5.55362500 | 2.11943600 |
| C | 5.12852000 | 0.91635100 | 0.51933800 |
| H | 6.18225800 | 0.58078100 | 0.44975200 |
| H | 4.52055400 | 0.07064500 | 0.87987000 |
| H | 5.07560100 | 1.70394300 | 1.29184200 |
| C | 4.22398600 | -1.78213700 | -2.68702200 |
| H | 5.24402700 | -1.72249500 | -3.11746300 |
| H | 3.72149500 | -0.81844500 | -2.86257900 |
| H | 3.66912800 | -2.54411900 | -3.26121900 |
| C | -2.78063200 | -3.86241700 | 3.15940400 |
| H | -2.79092100 | -4.35792600 | 4.13916000 |
| C | -4.27479100 | 2.16729800 | 3.84003900 |
| H | -4.64486900 | 2.19189000 | 4.87352400 |
| C | -4.89148700 | 3.39703600 | -1.79598800 |
| H | -5.68997200 | 3.30796100 | -2.56105700 |
| H | -4.28159800 | 4.27668900 | -2.07082200 |
| H | -5.38828800 | 3.60972700 | -0.83556000 |
| C | -4.20843900 | 3.11304600 | 1.59933200 |
| H | -4.51508200 | 3.90908000 | 0.91234400 |
| C | -2.20755300 | -2.03308000 | -3.70500700 |
| H | -1.67871400 | -2.58674400 | -4.50447200 |
| H | -1.84797900 | -0.99117300 | -3.74703200 |
| H | -3.28524300 | -2.04067200 | -3.95058900 |
| C | -5.22512800 | -2.66394000 | -1.88794300 |
| H | -6.28374300 | -2.39911400 | -2.08825400 |
| H | -5.23515600 | -3.48271200 | -1.14679000 |
| H | -4.80315400 | -3.05346600 | -2.82872300 |
| C | -3.62555900 | 1.70482700 | -3.17814200 |
| H | -4.50977600 | 1.54915300 | -3.82893800 |
| H | -3.03293800 | 0.77391000 | -3.17420900 |
| H | -3.00370400 | 2.48609100 | -3.64842500 |
| C | 2.67919600 | -1.02357900 | 3.70469400 |
| H | 2.21971200 | -0.24439500 | 4.32600700 |
| C | 2.48176200 | 4.25707400 | -2.21972900 |
| H | 2.07272000 | 4.72270000 | -3.13898900 |
| H | 3.53741000 | 4.57334700 | -2.13906900 |
| H | 1.92746400 | 4.67384300 | -1.36334800 |
| C | 3.47721000 | -2.00664200 | 4.30886800 |
| H | 3.65681300 | -1.98771800 | 5.39181800 |
| C | 1.65071500 | -4.09942100 | -1.97656800 |
| H | 1.08061700 | -5.04714300 | -2.03789900 |
| H | 2.58342400 | -4.23889500 | -2.54993600 |
| H | 1.06348300 | -3.31749000 | -2.48817100 |
| C | 4.02546100 | -3.03290700 | 3.52186900 |
| H | 4.62735700 | -3.82450700 | 3.98647600 |
| C | 2.97353200 | 2.17662600 | -3.60004500 |
| H | 2.53930100 | 2.68302300 | -4.48421500 |
| H | 2.79036200 | 1.09768400 | -3.72209900 |
| H | 4.06374200 | 2.35082600 | -3.62817200 |
| C | 5.48501700 | 2.70345900 | -1.19684900 |
| H | 6.55973700 | 2.43007700 | -1.21636900 |
| H | 5.36976800 | 3.49590300 | -0.43699300 |

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|---|---|---|---|
| H | 5.23655100 | 3.13101000 | -2.18127900 |
| C | -4.68557900 | 3.14612100 | 2.92134100 |
| H | -5.37416900 | 3.94223400 | 3.23318900 |
| C | -1.34964100 | 4.06372500 | -2.05809600 |
| H | -0.75142300 | 4.99594700 | -2.03846900 |
| H | -2.16389000 | 4.20939700 | -2.78916100 |
| H | -0.69966400 | 3.25452700 | -2.43840600 |
| H | 0.16746600 | 1.03535600 | -0.93933500 |
| H | -0.09752000 | -0.98643500 | -0.39159300 |

**4-$(N_2)_2$** (S = 1/2)

| | | | |
|---|---|---|---|
| Fe | -1.40629400 | 0.19224900 | -0.78986300 |
| Fe | 1.40623600 | -0.19232300 | -0.78988600 |
| P | 2.65623700 | 1.68570000 | -0.88953700 |
| P | -2.73002100 | 1.90822900 | -0.27683100 |
| P | 2.73006300 | -1.90826400 | -0.27688300 |
| P | -2.65638200 | -1.68567800 | -0.88941100 |
| Si | 1.43415000 | 0.20705600 | 1.42775800 |
| Si | -1.43399900 | -0.20708400 | 1.42777500 |
| O | 0.00009400 | -0.00008300 | 2.32955100 |
| C | 1.95456100 | 2.01705200 | 1.77415300 |
| N | -1.30244700 | 0.60404600 | -2.52287700 |
| C | 2.09915800 | -3.69804500 | -0.45548900 |
| H | 2.91336800 | -4.35383700 | -0.08570500 |
| C | 2.51088800 | 2.71618700 | 0.67357000 |
| C | 2.68762000 | -0.92976900 | 2.33582600 |
| C | -2.09917400 | 3.69801100 | -0.45559600 |
| H | -2.91334900 | 4.35379100 | -0.08571400 |
| C | -1.95446100 | -2.01705800 | 1.77421200 |
| C | -4.44432300 | 2.02477700 | -1.17626800 |
| H | -5.01058900 | 1.20578600 | -0.69710000 |
| C | -2.51086200 | -2.71619200 | 0.67366600 |
| C | 2.95931700 | 4.04641200 | 0.84590900 |
| H | 3.39653600 | 4.60500000 | 0.01348400 |
| C | 4.44427200 | -2.02488600 | -1.17649700 |
| H | 5.01062400 | -1.20592200 | -0.69738500 |
| C | -3.22594700 | 1.97073500 | 1.53879000 |
| C | 4.57391100 | 1.64746900 | -1.04072300 |
| H | 4.74418600 | 0.86183700 | -1.79946600 |
| C | -4.57408600 | -1.64741600 | -1.04029000 |
| H | -4.74447400 | -0.86180000 | -1.79902400 |
| C | 2.05247000 | 2.75720500 | -2.35783000 |
| H | 0.97916800 | 2.49037700 | -2.35810400 |
| C | 1.81615400 | 2.68388700 | 3.01097400 |
| H | 1.34029900 | 2.16015800 | 3.84992000 |
| C | -2.68730800 | 0.92985800 | 2.33592300 |
| C | -1.81598200 | -2.68388500 | 3.01102800 |
| H | -1.34006700 | -2.16015500 | 3.84993800 |
| C | 3.22620400 | -1.97066700 | 1.53868400 |
| C | 3.00085200 | -0.89048300 | 3.71192400 |

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|---|---|---|---|
| H | 2.58576200 | -0.08799500 | 4.33499800 |
| C | -0.86960200 | 3.89918200 | 0.43837500 |
| H | -0.51080000 | 4.94492100 | 0.37162900 |
| H | -0.04860600 | 3.23379700 | 0.12613900 |
| H | -1.08403400 | 3.67875500 | 1.49755400 |
| C | -2.95929200 | -4.04641200 | 0.84604400 |
| H | -3.39657300 | -4.60500300 | 0.01365600 |
| C | 5.17806400 | 1.18149900 | 0.29842000 |
| H | 6.23782100 | 0.88914700 | 0.16134200 |
| H | 4.63759700 | 0.32590600 | 0.73632300 |
| H | 5.14684400 | 1.99775600 | 1.04166300 |
| C | -5.27351100 | 3.31353400 | -0.99976600 |
| H | -6.21921000 | 3.22297600 | -1.57165700 |
| H | -4.74910500 | 4.20564800 | -1.38773000 |
| H | -5.54963500 | 3.50188100 | 0.04930900 |
| C | -2.24860800 | -4.00842500 | 3.17450800 |
| H | -2.13172500 | -4.51580000 | 4.14102700 |
| C | 2.13919800 | 4.29271700 | -2.28903600 |
| H | 1.63996600 | 4.72108200 | -3.18088900 |
| H | 3.18117600 | 4.66046500 | -2.29163400 |
| H | 1.63039800 | 4.69654800 | -1.39899700 |
| C | -2.05289800 | -2.75716800 | -2.35783700 |
| H | -0.97959600 | -2.49034600 | -2.35833800 |
| C | -2.82946200 | -4.68649200 | 2.08981700 |
| H | -3.17284300 | -5.72244400 | 2.20622900 |
| C | -4.00957300 | 2.97814400 | 2.14482000 |
| H | -4.36862500 | 3.83536900 | 1.56586800 |
| N | -1.20072400 | 0.95455500 | -3.61628300 |
| C | 0.86969100 | -3.89916600 | 0.43864200 |
| H | 0.51085500 | -4.94489700 | 0.37195100 |
| H | 0.04866600 | -3.23377200 | 0.12649600 |
| H | 1.08426200 | -3.67873900 | 1.49779100 |
| C | 2.82956100 | 4.68649800 | 2.08968700 |
| H | 3.17294200 | 5.72245300 | 2.20607400 |
| C | -5.17801700 | -1.18141400 | 0.29894200 |
| H | -6.23779200 | -0.88904500 | 0.16203300 |
| H | -4.63746500 | -0.32582200 | 0.73674600 |
| H | -5.14668800 | -1.99765800 | 1.04219300 |
| C | -4.34214000 | 1.69539400 | -2.67988700 |
| H | -5.36053700 | 1.61550700 | -3.11074500 |
| H | -3.81502700 | 0.74895000 | -2.86977900 |
| H | -3.80521700 | 2.47726200 | -3.24370500 |
| C | 2.24877800 | 4.00843100 | 3.17441700 |
| H | 2.13194900 | 4.51581200 | 4.14093900 |
| C | 3.81814100 | -1.86726400 | 4.30089300 |
| H | 4.05454400 | -1.82139800 | 5.37201600 |
| C | 5.27341300 | -3.31368600 | -1.00008800 |
| H | 6.21906000 | -3.22316500 | -1.57207100 |
| H | 4.74892400 | -4.20576500 | -1.38802100 |
| H | 5.54963400 | -3.50207200 | 0.04895400 |
| C | 4.00994000 | -2.97801300 | 2.14467500 |
| H | 4.36894400 | -3.83526100 | 1.56573000 |

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|---|---|---|---|
| C | 2.63502600 | 2.22967400 | -3.68539600 |
| H | 2.09227500 | 2.68941700 | -4.53329200 |
| H | 2.52059700 | 1.13991200 | -3.78285100 |
| H | 3.70413900 | 2.48150300 | -3.80288700 |
| C | 5.31147700 | 2.92218800 | -1.49524700 |
| H | 6.39727100 | 2.71113400 | -1.57611100 |
| H | 5.19725900 | 3.73390300 | -0.75560200 |
| H | 4.97634600 | 3.29816100 | -2.47506300 |
| C | 4.34199100 | -1.69550300 | -2.68010900 |
| H | 5.36036000 | -1.61580500 | -3.11106800 |
| H | 3.81503400 | -0.74896600 | -2.86996200 |
| H | 3.80487000 | -2.47728100 | -3.24386200 |
| C | -3.00035900 | 0.89067100 | 3.71206500 |
| H | -2.58521100 | 0.08821000 | 4.33513500 |
| C | -2.13958100 | -4.29268400 | -2.28904200 |
| H | -1.64052300 | -4.72102400 | -3.18100500 |
| H | -3.18154600 | -4.66047100 | -2.29142600 |
| H | -1.63057500 | -4.69650600 | -1.39911600 |
| C | -3.81753300 | 1.86751900 | 4.30108100 |
| H | -4.05379600 | 1.82172900 | 5.37223800 |
| C | -1.78832500 | 4.07559800 | -1.91336900 |
| H | -1.31241400 | 5.07526900 | -1.95250600 |
| H | -2.69328500 | 4.11417200 | -2.54326700 |
| H | -1.09580300 | 3.35189500 | -2.37529100 |
| C | -4.30994400 | 2.92279200 | 3.51574000 |
| H | -4.92253600 | 3.71145300 | 3.97114200 |
| C | -2.63573100 | -2.22961500 | -3.68527300 |
| H | -2.09325700 | -2.68945800 | -4.53329200 |
| H | -2.52118200 | -1.13987000 | -3.78278700 |
| H | -3.70490700 | -2.48130700 | -3.80248200 |
| C | -5.31173400 | -2.92213500 | -1.49468000 |
| H | -6.39754600 | -2.71108800 | -1.57532500 |
| H | -5.19735800 | -3.73385900 | -0.75507000 |
| H | -4.97679200 | -3.29809400 | -2.47456700 |
| C | 4.31048500 | -2.92256800 | 3.51555400 |
| H | 4.92316400 | -3.71118000 | 3.97092400 |
| C | 1.78808500 | -4.07564000 | -1.91321200 |
| H | 1.31217400 | -5.07531400 | -1.95227300 |
| H | 2.69294000 | -4.11420900 | -2.54326400 |
| H | 1.09548100 | -3.35194000 | -2.37501700 |
| H | -0.13152700 | -0.93786100 | -0.51757100 |
| H | 0.13099200 | 0.93768500 | -0.51683900 |
| N | 1.30238800 | -0.60417300 | -2.52289400 |
| N | 1.20066100 | -0.95477600 | -3.61626900 |

| Pre-catalyst | Equiv $H^+/e^-$ | Temperature | Order of Addition | Yield of $NH_3$ (molar equivalents) |
|---|---|---|---|---|
| **3-$N_2$** | 48 | -78 °C | Acid First | 1.56 |
| **3-$N_2$** | 48 | -78 °C | Acid First | 1.39 |
| **3-$N_2$** | 48 | -78 °C | Reductant First | 1.70 |
| **3-$N_2$** | 48 | -78 °C | Reductant First | 0.96 |
| **3-$N_2$** | 48 | -78 °C | Reductant First | 1.18 |
| **3-$N_2$** | 48 | -78 °C | Reductant First | 1.60 |
| **3-$N_2$** | 48 | 0 °C | Reductant First | 0.24 |
| **3-$N_2$** | 48 | 0 °C | Reductant First | 0.17 |
| **3-$N_2$** | 10 | -78 °C | Reductant First | 0.59 |
| **3-$N_2$** | 10 | -78 °C | Reductant First | 0.42 |
| **4-$(N_2)_2$** | 48 | -78 °C | Acid First | 1.27 |
| **4-$(N_2)_2$** | 48 | -78 °C | Acid First | 0.94 |

**Table S5**. $N_2$ reduction catalysis data.

# References


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